PB83-124719

Forced-Oxidation Demonstration at the TVA Widows Creek Unit 8 FGD System

Tennessee Valley Authority
Chattanooga

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

May 82

U.S. Department of Commerce
National Technical Information Service
NTIS

PB83-124719

TVA

Tennessee Valley
Authority
Office of Power

Energy Demonstrations
and Technology
Chattanooga, TN 37401

TVA/OP/EDT-82/15

EPA

United States
Environmental Protection
Agency

Industrial Environmental
Research Laboratory
Research Triangle Park, NC 27711

EPA-600/7-82-043
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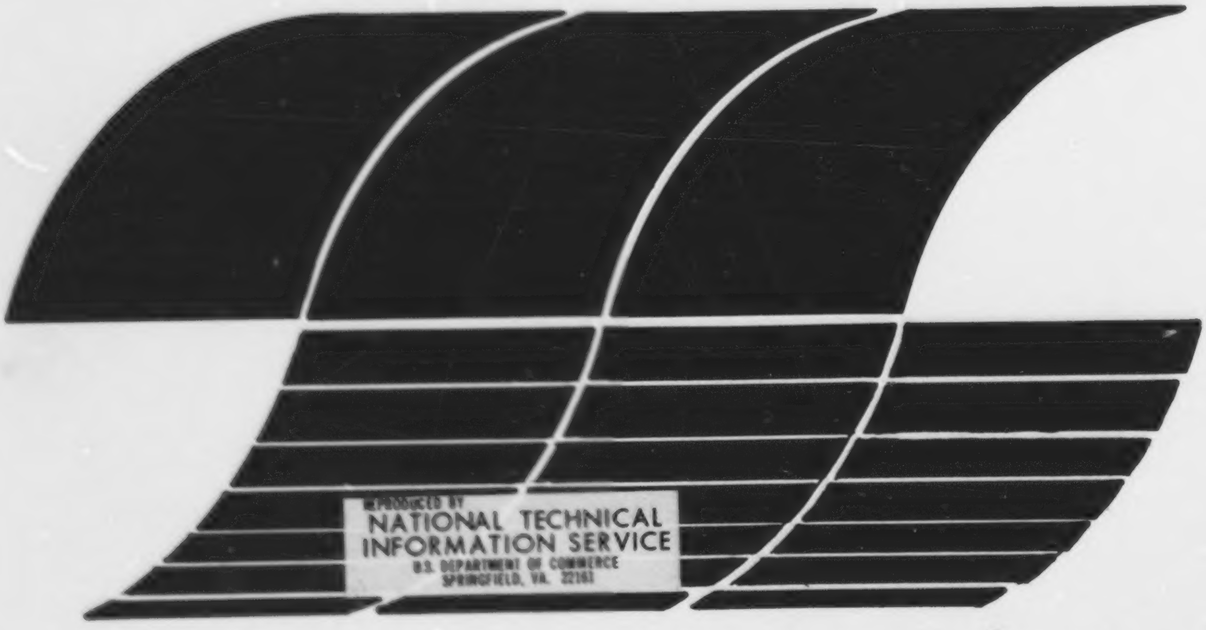
Interagency Energy/Environment R&D Program Report



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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-82-043	2.	3. RECIPIENT'S ACCESSION NO. PB83 124719
4. TITLE AND SUBTITLE Forced-oxidation Demonstration at the TVA Widows Creek Unit 8 FGD System		5. REPORT DATE May 1982
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) J. G. Patterson, G. T. Munson, R. A. Runyan, J. D. Veitch, and W. L. Wells		8. PERFORMING ORGANIZATION REPORT NO. TVA/OP/EDT-82/15
9. PERFORMING ORGANIZATION NAME AND ADDRESS TVA, Office of Power 1120 Chestnut Street, Tower II Chattanooga, Tennessee 37401		10. PROGRAM ELEMENT NO. INE827
		11. CONTRACT/GRANT NO. IAG-D9-E721-GH
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 4/78-11/81
		14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Julian W. Jones, Mail Drop 61, 919/541-2489.

16. ABSTRACT

The report discusses an evaluation by TVA of forced oxidation in a 140-MW train of the Widows Creek steam plant Unit 8 venturi-spray tower limestone FGD system. Oxidation by air sparging in the agitated hold tank of both the venturi and spray tower absorber consistently produced over 95% oxidation at air rates of 2 lb atoms O/lb mole SO_2 absorbed (stoichiometry of 2, or 100% excess). Oxidation only in the venturi hold tank produced less consistent results because of carryover mixing of the liquid in the two tanks. Oxidation levels above 95% permitted dewatering to over 80% solids using a thickener and rotary vacuum filter. The dewatered waste was easily handled as a solid. SO_2 removal and FGD system operating characteristics were unaffected. Forced oxidation appears to be a practical method of producing a solid waste that can be disposed of in a landfill (as an alternative to pond waste disposal) for the Unit 8 FGD system.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Calcium Carbonates	Pollution Control	13B	
Oxidation	Sulfur Oxides	Stationary Sources	07B,07C	
Earth Fills	Dewatering	Forced Oxidation	13C	13H
Waste Disposal				
Flue Gases			21B	
Desulfurization			07A,07D	

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 144
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

TVA/OP/EDT-82/15
EPA-600/7-82-043
May 1982

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EPA-IAG-D9-E721-GH

Program Element No. INE827

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Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

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NOTE

G. T. Munson is now in the Division of Fossil and Hydro Power, Office of Power, Tennessee Valley Authority, Chattanooga, Tennessee.

ABSTRACT

To assess landfill as an alternative to pond waste disposal TVA evaluated forced oxidation in a 140-MW train of the Widows Creek Steam Plant unit 8 venturi - spray tower limestone FGD system. Oxidation by air sparging in the agitated hold tanks of both the venturi and spray tower absorber consistently produced over 95% oxidation at combined total air rates of 2 lb atoms O/lb mole SO_2 absorbed. Oxidation only in the venturi hold tank produced less consistent results because of carryover mixing of the liquid in the two tanks. Also, lower air rates had to be used in the venturi hold tank because the tank was smaller. Oxidation levels above 95% permitted dewatering to over 80% solids using a thickener and rotary drum vacuum filter. The dewatered waste was easily handled as a solid. SO_2 removal and FGD system operating characteristics were unaffected. Forced oxidation appears to be a practical method of producing a solid waste in the unit 8 FGD system.

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ABBREVIATIONS AND CONVERSION FACTORS

ABBREVIATIONS

aft^3	actual cubic feet
Btu	British thermal unit
°F	degrees Fahrenheit
dia	diameter
ESP	electrostatic precipitator
FGD	flue gas desulfurization
ft	feet
gal	gallon
gr	grain
hp	horsepower
h	hour
hr	hour
in.	inch
J	Joule
k	10^3
kW	kilowatt
kWh	kilowatthour
L	liter
lb	pound
L/G	liquid-to-gas ratio
M	10^6
mi	mile
MW	megawatt
n	10^{-9}
Pa	pascal
ppm	parts per million
psig	pounds per square inch (gauge)
rpm	revolutions per minute
s	second
sec	second
sft^3	standard cubic feet (60°F)
yr	year

CONVERSION FACTORS

EPA policy is to express all measurements in agency documents in metric units. Most values in this report are given in British units for the convenience of those accustomed to using the British systems. Where used, metric convention follows the rates, conventions, and numerial factors of ASTM E 380. The following approximate conversion factors may be used to provide metric equivalents.

British			Metric	
acre	acre	0.405	hectare	ha
Btu	British thermal unit	1.055	kilojoule	kJ
Btu/lb	Btu per pound	2.526	kilojoules per kilogram	kJ/kg
°F	degrees Fahrenheit minus 32	0.556	degrees Celsius	°C
ft	feet	0.3048	meters	m
ft^2	square feet	0.0929	square meters	m^2
ft^3	cubic feet	0.02832	cubic meters	m^3
ft/min	feet per minute	0.00508	meters per second	m/s
ft^3/min	cubic feet per minute	0.000472	cubic meters per second	m^3/s
gal	gallons (U.S.)	3.785	liters	L
gal/min	gallons per minute	0.06308	liters per second	L/s
gal/kaft^3	gallons per thousand actual cubic feet	429.9	liters per actual cubic meter	L/m^3 (actual)
gr	grains	0.0648	grams	g
gr/ft^3	grains per cubic foot	2.288	grams per cubic meter	g/m^3
hp	horsepower	0.746	kilowatts	kW
in.	inches	2.54	centimeters	cm
in. H$_2$O	inches of water	25.4	millimeters of water	mm H$_2$O
lb	pounds	0.4536	kilograms	kg
lb/ft^3	pounds per cubic foot	16.02	kilograms per cubic meter	kg/m^3
lb/hr	pounds per hour	0.4536	kilograms per hour	kg/h
lb/MBtu	pounds per million Btu	429.9	nanograms per joule	ng/J
psia	pounds per square inch absolute	6.895	kilopascals	kPa
mi	miles	1.609	kilometers	km
sft^3/min	standard cubic feet per minute (60°F)	1.6077	normal cubic meters per hour (0°C)	m^3/h (0°C)
ton	tons (short)	0.9072	metric tons	tonne

FORCED-OXIDATION DEMONSTRATION AT THE TVA
WIDOWS CREEK UNIT 8 FGD SYSTEM

EXECUTIVE SUMMARY

INTRODUCTION

In the early 1970's TVA began efforts leading to installation of a full-scale limestone scrubbing FGD system on unit 8 of the Widows Creek Steam Plant near Stevenson, Alabama. The design was based in part on pilot-plant FGD studies. This system was intended to serve as a demonstration system to provide data that could be applied both to the unit 8 system and to possible future systems. At the time ponding appeared to be the most feasible waste disposal method. A 100-acre impoundment was constructed that was estimated to have a capacity for about seven years of operation. A larger pond was not considered, primarily because of the possibility that improved waste disposal methods would evolve by the time additional disposal capacity was needed. The FGD system was completed in 1977 and has operated successfully, fulfilling the objectives of its installation.

The unit 8 FGD system has now been incorporated into the overall TVA SO_2 emission control program for Widows Creek, which includes installation of a similar system on unit 7. Because of the increased quantity of waste that would result from implementation of these plans, it is estimated that existing pond capacity will be exhausted by the end of 1984, adding impetus to the development ot an alternate disposal method. Various landfill methods involving stabilization of the high-sulfite sludge were studied but did not appear promising for the Widows Creek situation. Insufficient dry fly ash was available to ensure adequate stabilization.

Modification of the FGD systems to permit forced oxidation of calcium sulfite to gypsum was also considered as a method of producing a waste suitable for landfill. To evaluate this possibility TVA contracted with Combustion Engineering, Inc., to install and operate a prototype forced-oxidation and dewatering system on the unit 8 FGD system. Because the project would provide additional information for their already extensive studies in limestone forced-oxidation FGD, EPA provided partial funding for the evaluation and publication of the results. Tests simulating unit 8 conditions were also conducted at the Shawnee test facility using TVA funds. The forced-oxidation system, consisting of air sparging equipment, was installed on one of the four absorber trains of the unit 8 FGD system. A thickener and rotary filter were installed to process about 10% of the absorber waste stream. The objective was to produce a waste composed of 95% gypsum that could be dewatered to 80% or more solids. The demonstration program began in April 1979 and continued until January 1980. Until June 1979 the program was conducted by the C-E Environmental Systems Division of Combustion Engineering with Radian Corporation providing sampling and analytical support. After June 1979 the program was conducted by Radian.

This report discusses the background of limestone forced-oxidation FGD as it pertains to the unit 8 demonstration program and presents the results of the test program. Portions of this report, including all of the numerical data, were provided in an unpublished report to TVA by C-E Environmental Systems and in an unpublished report to TVA by Radian.

POWER PLANT AND EQUIPMENT DESCRIPTION

The Widows Creek 550-MW unit 8 has a dry-bottom, tangentially fired double furnace, each with two flue gas ducts. ID fans in each duct also serve as FD fans for the FGD system. The ESP's remove less than 50% of the fly ash in the flue gas. The boiler burns bituminous coal containing 4% sulfur and 20% ash.

The unit 8 FGD system consists of four identical FGD trains, one for each flue gas duct, that scrub all of the flue gas from the boiler (1,620,000 ft^3/min at 260°F at full load). One train, train D, was modified for the forced-oxidation test. The modifications consisted of installation of higher powered turbine agitators in the venturi and absorber hold tanks and air sparging manifolds beneath both agitators. A thickener and a rotary filter were installed to process about one-tenth of the effluent from train D. The FGD train consists of a venturi - spray tower absorber combination with separate, agitated hold tanks. Flue gas passes downward through the venturi, through the chamber connecting the venturi and spray tower, then upward through the spray tower. The flue gas then passes through a vertical mist eliminator and into a chamber where it is heated to 175°F by mixing it with heated air and vented to the stack. Slurry is recirculated through the venturi and absorber from their respective hold tanks. Fresh limestone slurry (90% to pass 200 mesh at about 60% solids) is added to the absorber hold tank. The absorber hold tank overflows to the venturi hold tank, which overflows to the effluent tank from which it is pumped to the pond. The effluent slurry normally contains about 12% solids, of which about 30% is fly ash. Without forced oxidation the sulfur species are about 70% sulfite and 30% sulfate.

The venturi has a variable rectangular throat designed for a pressure drop of 5 inches H_2O although it often operates at higher pressure drops of about 10 inches H_2O. The normal slurry recirculation rate provides an L/G ratio of about 10 gal/kft^3. The venturi hold tank has a diameter of 18 feet and is 25 feet high. It was equipped for the test with a constant-speed, 75-horsepower, turbine-blade agitator that originally operated at 45 rpm, later increased to 56 rpm. The retention time is 12 minutes based on recirculation and 150 minutes based on effluent flow rate. The venturi is designed to reduce the approximately 6 gr/sft^3 of fly ash in the flue gas to a maximum of 0.06 gr/sft^3. It also removes some of the SO_2 in the flue gas.

The absorber is 30 feet by 16 feet in cross section and 34 feet high. It contains five trays of multigrids, primarily intended to improve flue gas distribution. An array of low-pressure nozzles distributes the absorbent above the top tray. The pressure drop is 3 to 4 inches H_2O. The design removal efficiency is about 70% in the original configuration. The normal slurry recirculation rate is 20,000 gal/min, corresponding to an L/G ratio of 60 gal/kft^3. The absorber hold tank has a diameter of 33 feet, is 25 feet high, and has a capacity of 150,400 gallons. It was equipped with a constant-speed, 300-horsepower, 68-rpm, turbine agitator for the test. The retention time in the hold tank is 7.5 minutes, based on recirculation rate, and 280 minutes based on effluent rate.

Although the venturi and absorber have separate hold tanks with series flow of absorbent from the absorber tank to the venturi tank, there is a considerable carryover of entrained absorbent from the venturi to the absorber. The effect is to reduce the differentiation of chemical properties between the absorbent in the two hold tanks. The lower venturi-loop pH, which favors oxidation, could not be attained to the full extent.

Oxidation air was introduced to the hold tanks through annular manifolds mounted directly beneath the agitator turbines. Compressed air was supplied by 11 screw-type compressors with a total capacity of 8,550 ft^3/min at 100 psig.

The thickener had a diameter of 20 feet, was 8 feet deep, and had a scraper blade driven at about 0.2 rpm. An automatic polyelectrolyte flocculent system was used. The vacuum filter contained a drum 4-1/2 feet in diameter and 6 feet long divided into 12 compartments. The filter cloth was Dacron. The drum operated with 30% to 40% of the circumference submerged in an agitated vat. The filter cake, normally 1/4 to 1-1/4 inches thick, was removed by reverse air flow and a scraper blade. About 25% of the filter was blanked with shellac because the filter was oversized for the available flow rates.

TEST OBJECTIVES, TEST PLAN, AND OPERATING CONDITIONS

The general objectives of the Widows Creek forced-oxidation test were to demonstrate forced oxidation as a practical method of producing a gypsum waste suitable for landfill disposal and to acquire the data needed to design full-scale systems on units 7 and 8. The specific goals were to attain a minimum of 95% oxidation and a waste that could be dewatered to at least 80% solids over a range of conditions sufficient to define the optimum design and operating conditions, within the requirements of the 88% SO_2 removal to be required for units 7 and 8. The test plan, based on available data within TVA, operating experience at the Shawnee test facility, and published work, consisted of three series of tests: A series - Oxidation in the absorber hold tank, B series - Oxidation in the venturi hold tank, and C series - Oxidation in both the absorber and venturi hold tanks. (A D series was added during the test period to denote a different waste disposal method. Operating conditions for the D series did not differ from the C series.) These three oxidation modes would demonstrate venturi hold tank and absorber hold tank forced oxidation as well as a combination of both, allowing a determination of the method best suited to the Widows Creek system. A primary criterion, in addition to attaining the oxidation and dewatering goals, was the minimum air stoichiometry attainable under each of the three oxidation modes. Since the dewatering system objectives could be determined without treatment of the full effluent stream, a dewatering system to treat 10% of the effluent was specified.

The A series was rescheduled and eventually dropped because the B series appeared to offer the best possibility of efficient oxidation at the minimum air stoichiometry. When this did not prove wholly satisfactory, probably because of mixing between the two hold tanks due to carryover in the flue gas, the remainder of the test period was devoted to the C series of tests (including those designated D series).

The test conditions differed from the test plan conditions based on full-load operation in some respects. The actual flue gas rates were lower and generally fluctuated throughout the test period because of the load-following nature of the power unit operation. The SO_2 content of the flue gas was low because coal with lower than normal sulfur was being used. Limestone stoichiometry varied with normal operating procedures to control the venturi hold tank pH at a fixed level. The air stoichiometries of the first B-series tests were low because of limitations in the air system. Subsequently, the air stoichiometries were limited by the stress that could be placed on the hold tank agitator.

RESULTS

The two phases of study in the Widows Creek forced-oxidation demonstration test were forced oxidation and dewatering of the resulting waste slurry. The forced-oxidation phase was primarily concerned with definition of oxidation level in terms of the oxidation configuration and air stoichiometry while the dewatering phase was primarily concerned with definition of the dewatering characteristics in terms of the oxidation level.

Forced Oxidation

A summary of operating conditions and average results for steady-state run conditions is shown in Table S-1. Average analytical data on bleedstream and thickener underflow are shown for the same runs in Tables S-2 and S-3. All B-series tests were run with oxidation air sparged only into the venturi hold tank. All C- and D-series tests were run with air sparged into both the venturi hold tank and the absorber hold tank. The D designation denotes a different disposal method to evaluate a test landfill.

The tables show the lower than expected rates and variable nature of the flue gas flow. The flue gas SO_2 content ranged from about 1,300 to 2,400 ppm, but was usually in the 1,700 to 2,000 ppm range. Limestone stoichiometry

TABLE S-1. TEST DATA SUMMARY

Test	Date	Flue gas, kft3/min[a]	SO_2 removal, %	Air stoichiometry[b]	Oxidation, %	Filter cake solids, %	Limestone stoichiometry[c]
B-2	4/30-5/1	270	75	0.8	63	68	1.3
B-2A	5/8-5/16	300	81	1.8	80	76	1.2
B-2	5/25-5/26	270	79	1.9	79	70	1.2
B-2B	5/31	270	79	2.4	91	-	1.2
C-1	6/27-6/29	390	84	2.8	99	82	1.5
C-2A	8/9-8/12	308	85	2.1	99	82	1.1
C-2B	8/19-8/20	334	-	2.1	96	-	2.0
C-2D	8/26-9/1	317	84	1.9	97	-	1.4
C-2E	9/4-9/9	327	83	1.9	90	-	1.5
C-2F	9/19-9/22	345	81	1.8	95	86	1.6
C-2G	9/24-9/25	326	81	1.7	96	76	1.1
C-2H	10/1-10/2	274	-	1.9	95	-	1.1
C-2	10/26-11/2	-	-	2.0	96	-	1.6
C-2T	10/30-11/2	305	89	1.7	99	-	1.8
D-1	11/12-11/16	295	-	1.9	99	87	1.8
D-2	11/17-11/20	296	-	1.7	99	-	1.7
D-4	12/3-12/14	337	87	1.8	98	89	1.3
D-5	12/17-12/21	324	89	2.4	99	88	1.3
D-6	1/2-1/5	300	90	-	99	90	1.3

a. 1 atm, 280°F.

b. lb atoms O/lb moles SO_2 removed ($2SO_3^= + O_2 \rightarrow 2SO_4^=$).

c. lb moles $CaCO_3$/lb mole SO_2 removed.

TABLE S-2. BLEEDSTREAM ANALYTICAL DATA SUMMARY

		Liquid					Solids			
			mg/L		Relative saturation		mg/g			
Test	Date	pH	SO_3^{2-}	SO_4^{2-}	SO_3^{2-}	SO_4^{2-}	SO_3^{2-}	SO_4^{2-}	Acid insol.	Oxidation, %
No oxidation	5/21	5.1	507	1,790	2.7	1.0	-	-	-	39
B-2	4/30-5/1	5.9	140	1,200	1.8	1.2	110	211	310	62
B-2A	5/8-5/16	5.6	163	1,790	1.4	1.0	56	265	326	80
B-2	5/25-5/26	5.7	159	1,710	1.7	1.0	75	312	264	78
B-2B	5/31	5.5	140	1,560	1.2	0.9	28	348	270	91
C-1	6/27-6/29	5.8	5	1,630	0.7	1.0	1	306	367	99+
C-2A	8/9-8/12	5.6	890	1,360	3.2	0.9	4	310	292	99
C-2B	8/19-8/20	5.4	850	1,590	4.7	0.9	8	282	191	97
C-2D	8/26-9/1	5.2	852	1,470	3.8	0.9	9	321	243	97
C-2E	9/4-9/9	5.3	933	1,600	4.7	0.9	26	283	248	90
C-2F	9/19-9/22	5.4	191	1,670	1.0	0.9	14	327	273	95
C-2G	9/24-9/25	5.4	404	2,240	3.7	1.3	18	326	364	93
C-2H	10/1-10/2	5.1	-	2,080	0.0	0.9	12	345	294	95
C-2T	10/30-11/2	5.3	608	1,639	3.2	0.9	1	285	250	99
D-1	11/12-11/16	5.1	843	1,624	2.9	1.0	2	275	263	99
D-2	11/17-11/20	5.8	644	1,739	2.5	1.0	3	185	260	99
D-4	12/3-12/14	5.6	117	1,723	.9	1.0	7	312	285	98
D-5	12/17-12/21	5.8	85	1,619	1.1	0.9	6	300	228	98
D-6	1/2-1/5	5.6	793	1,739	6.4	0.9	2	345	-	99

TABLE S-3. THICKENER UNDERFLOW ANALYTICAL DATA SUMMARY

			Solids, mg/L			
Test	Date	pH	SO_3^{2-}	SO_4^{2-}	Acid insol.	Oxidation, %
B-2	4/30-5/1	6.3	78	205	309	69
B-2A	5/8-5/16	5.8	51	250	331	80
B-2	5/25-5/26	6.1	61	313	248	81
B-2B	5/31	6.5	32	341	245	90
C-1	6/27-6/29	6.3	0	298	356	100
C-2A	8/9-8/12	-	26	280	322	-
C-2B	8/19-8/20	-	7	293	198	-
C-2C	8/27	-	42	265	309	-
C-2D	8/26-9/1	-	7	264	259	-
C-2E	9/4-9/9	-	57	280	257	-
C-2F	9/19-9/22	-	12	293	255	-
C-2G	9/24-9/25	-	34	334	378	-
C-2H	10/1-10/2	-	12	354	302	-
C-2T	10/30-11/2	-	-	-	-	-
D-1	11/12-11/16	-	2	292	218	-
D-2	11/17-11/20	-	2	271	223	-
D-4	12/3-12/14	-	5	310	250	-
D-5	12/17-12/21	-	7	317	219	-
D-6	1/2-1/5	-	-	-	-	-

varied from 1.1 to 2.0 mol $CaCO_3$/mol SO_2 absorbed. Solids in the recirculated liquid also varied widely, ranging from 4% to 30% in the venturi loop. Stoichiometry and solids had no apparent effect on oxidation. The pH of the bleedstream was generally between 5.4 and 5.8. This pH probably represents the approximate oxidation conditions in the venturi loop. The bleedstream magnesium content was generally in the range of 200 to 500 mg/L and the chloride level was generally in the range of 500 to 1,800 mg/L. These are roughly compensating concentrations in terms of their effect on SO_2 removal. Relative saturations were low for both $CaSO_3 \cdot 1/2H_2O$ and $CaSO_4 \cdot 2H_2O$. There was no precise relationship between $CaSO_3 \cdot 1/2H_2O$ saturation and degree of oxidation. Unsaturated operation with respect to $CaSO_4 \cdot 2H_2O$ was the rule in the C- and D-series with two-tank oxidation. As with $CaSO_3 \cdot 1/2H_2O$ relative saturation, $CaSO_4 \cdot 2H_2O$ relative saturation showed no relationship to oxidation levels.

SO_2 removal efficiencies were generally in the range of 80% to 90% during the test program. During the latter stages of the program additional packing placed in the absorber increased the SO_2 removal efficiency into the 85% to 90% range. There was no indication that forced oxidation affected SO_2 removal efficiency or that, conversely, SO_2 removal efficiency affected forced oxidation.

The 0.4 to 0.8 air stoichiometries (all air stoichiometries are expressed as lb atoms O/lb mole SO_2 absorbed) of the early B series, which were limited by the original air metering system, produced at most about 60% oxidation. Tests with air stoichiometries of about 1.5 produced about 60% to 80% oxidation. In other B-series tests, with air stoichiometries between 1.7 and 2.8, oxidation ranged from 72% to 99%. There was a definite general trend of increasing oxidation efficiency with increasing air stoichiometry, however, as shown in Figure S-1. Oxidation rates were responsive to air stoichiometries but were also influenced by other undefined factors.

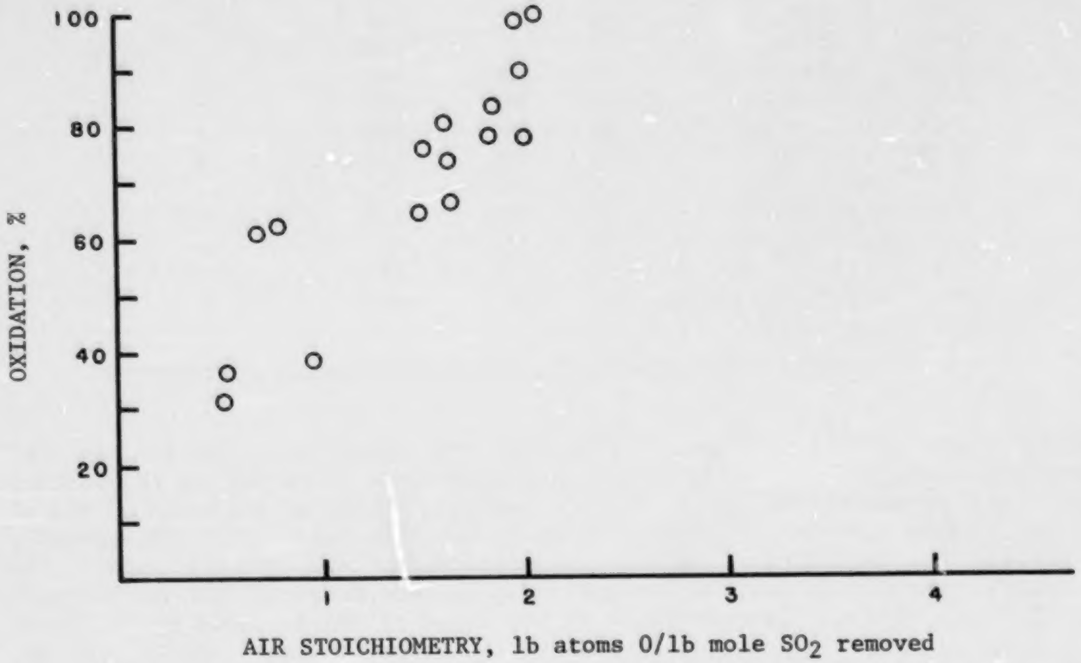


Figure S-1. Air stoichiometry versus percent oxidation, venturi tank oxidation (B series tests).

Air stoichiometries in the C- and D-series of tests ranged from 1.6 to 2.8, with most in the range of 1.7 to 2.0. As shown in Figure S-2, air stoichiometries of 1.6 to 2.8 all produced oxidation levels of 99% or more, while the range 1.6 to 2.0 also produced oxidation levels between 90% and 95%. Above an air stoichiometry of 2.0 oxidation levels were above 95%. Oxidation levels approaching 100% were, in fact, easily attained over an appreciable range of air stoichiometries. Most or all of the oxidation occurred in the absorber hold tank.

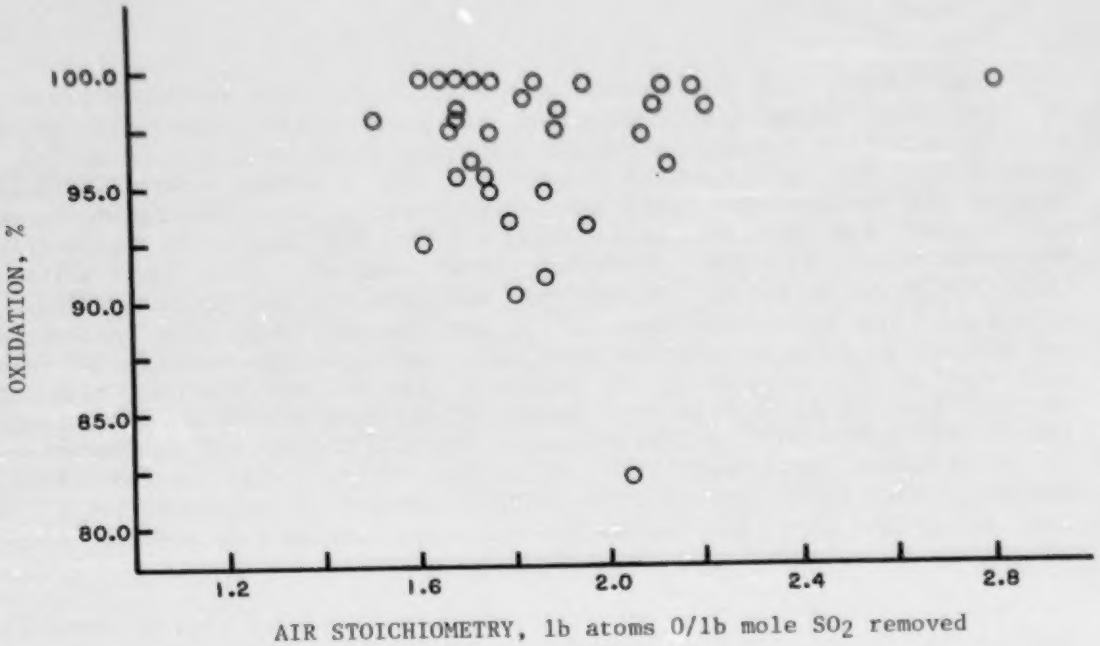


Figure S-2. Air stoichiometry versus oxidation level, two-tank oxidation (C and D series tests).

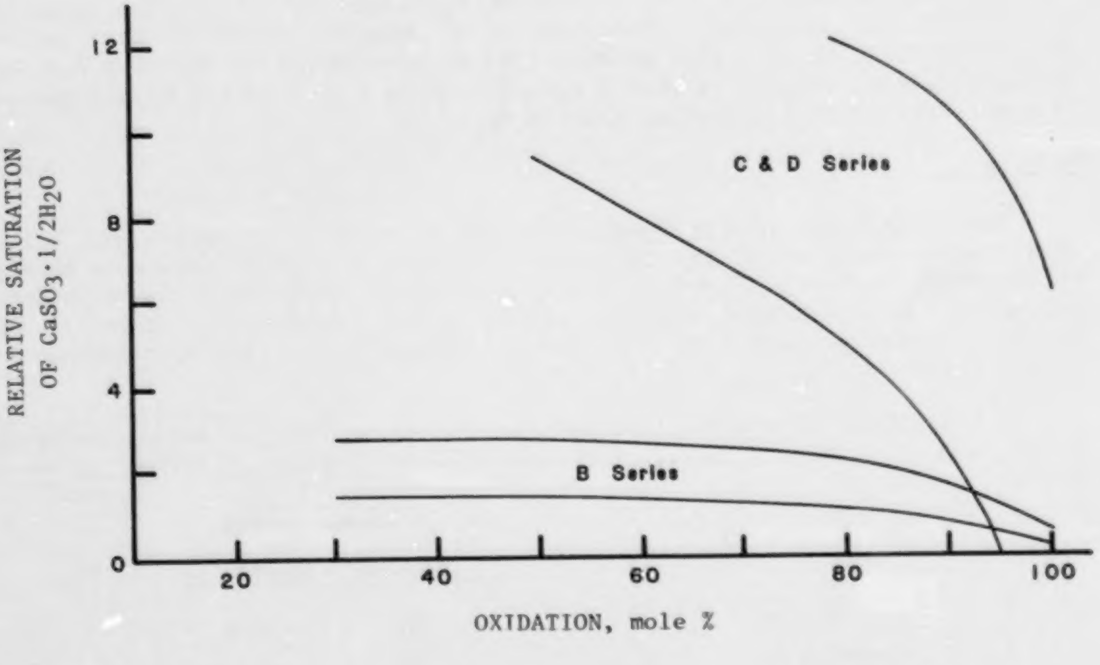


Figure S-3. Relative sulfite saturation versus oxidation level (Reference 9).

Measured SO_3^{2-} and SO_4^{2-} concentrations in the absorber and bleedstream are an indication of various dissolution and precipitation mechanisms in the overall oxidation process. Figure S-3 summarizes relative saturation of $CaSO_3 \cdot 1/2H_2O$ versus oxidation level for the B-series tests (oxidation only in the venturi hold tank) and C- and D-series tests (oxidation in both the venturi and absorber hold tanks). The low levels of $CaSO_3 \cdot 1/2H_2O$ supersaturation in the B-series tests suggest that dissolution of $CaSO_3 \cdot 1/2H_2O$ was occurring and that this mechanism was the source of HSO_3^- in solution. The relatively high pH of the venturi hold tank undoubtedly contributed to a low dissolution rate and a corresponding depletion of sulfur (IV) species in solution. In contrast, the C- and D-series tests are characterized by relatively high levels of supersaturation at low oxidation levels, which decreased as the oxidation level increased and approached zero as the oxidation level approached 100%. This suggests that at least some of the HSO_3^- formed in the absorber was oxidized without being precipitated. The low, often less than one, $CaSO_4 \cdot 2H_2O$ relative saturations suggest no rate limitation due to $CaSO_4 \cdot 2H_2O$ crystallization.

The results of the B-series tests and tests C-1 were used by Combustion Engineering to calculate an overall mass-transfer coefficient, K_La, which was then used to predict oxidation rates. The comparison shows a fair agreement between the predicted and actual values in most cases. A comparison of predicted air stoichiometries (developed from the same equations) with actual air stoichiometries shows less agreement. Radian also applied several models based on mass-transfer- and oxidation-rate-based derivations to the Widows Creek data. Oxidation rate and oxidation level show no correlation with air stoichiometry. The calculated K_ga shows no correlation with the superficial air velocity. The results do suggest, however, that an air stoichiometry of about 2 will produce 95% or more oxidation and that K_ga does not vary widely, suggesting that a K_ga of 8 to 10 x 10^{-6} lb-mol O_2/min-ft^3-psi O_2 represents typical operating conditions.

Dewatering

The evaluation of the dewatering characteristics of the waste stream consisted of operation of the thickener-filtration system to dewater a portion of the waste stream and various tests to further characterize the dewatering properties of the waste slurry. These tests consisted of chemical and physical characterization of the solids, settling rate determinations, and filter leaf tests.

A comparison of compositions and crystal sizes for the solids in Widows Creek unit 8 wastes produced with and without forced oxidation is shown below.

	Wt % of solids	
	No forced oxidation	Forced oxidation
$CaSO_3 \cdot 1/2H_2O$	31	0.9
$CaSO_4 \cdot 2H_2O$	24	56
$CaCO_3$	16	14
Limestone and fly ash inerts	28	27

Based on scanning electron microscope photographs, about 80% of the small, platey crystals of $CaSO_3 \cdot 1/2H_2O$ that predominate in the unoxidized waste are smaller than 20 micrometers. In contrast, about 80% of the blocky $CaSO_4 \cdot 2H_2O$ crystals in the highly oxidized waste are between 20 and 100 micrometers. The typical chemical properties of the oxidized waste for runs where oxidation over 95% are:

Oxidation, %	98
Solids, %	85
Ca/S ratio	1.46
Solids, mg/g	
$SO_3^=$	5.57
$SO_4^=$	312.0
$CO_3^=$	88.2
Ca^{++}	184.0
Mg^{++}	2.46
Inerts	274.0

The waste was so easily dewatered that the thickener and filter proved to be too large for the volume of waste obtainable in the sidestream and data near capacity rates could not be attained. The thickener was adequate for all flow rates and settling conditions and the overflow was always essentially free of solids. The filter had to be operated at a low vacuum to accept the low slurry flow rates. The maximum solids loading attainable was 50 to 70 lb/hr-ft^2, far below capacity. Figure S-4 shows the relationship of filter cake solids to oxidation level. Filter cake solids above 80% were usually attained at oxidation levels above 90%. At nearly complete oxidation levels, filter cake solids up to 90% were attained.

Graduate-cylinder settling rate tests were performed on a bleedstream sample at all steady-state conditions. The settling rate as a function of oxidation level is shown in Figure S-5. The settling rate remained fairly low up to an oxidation level of about 80% to 90%. It then increased several fold between 90% and 100% oxidation. The variation in settling rate at the higher oxidation levels is partially due to experimental error; some variation is also probably due to the variable limestone and fly ash content. The results indicate that a thickener unit area requirement of about 2 ft^2/ton-day is necessary for thickening of highly oxidized sludge in the free settling area (up to about 40% solids).

Filter leaf tests were made on slurry from the B-series and early C-series tests. In general, cake solids over 80% were attained at oxidation levels over 90%. In most cases the cake solids were in good agreement with rotary filter cake solids. The general agreement of the two data sets encourages confidence in laboratory tests as an indication of actual filter performance, even though the vacuum filter was operated off design rates (see above).

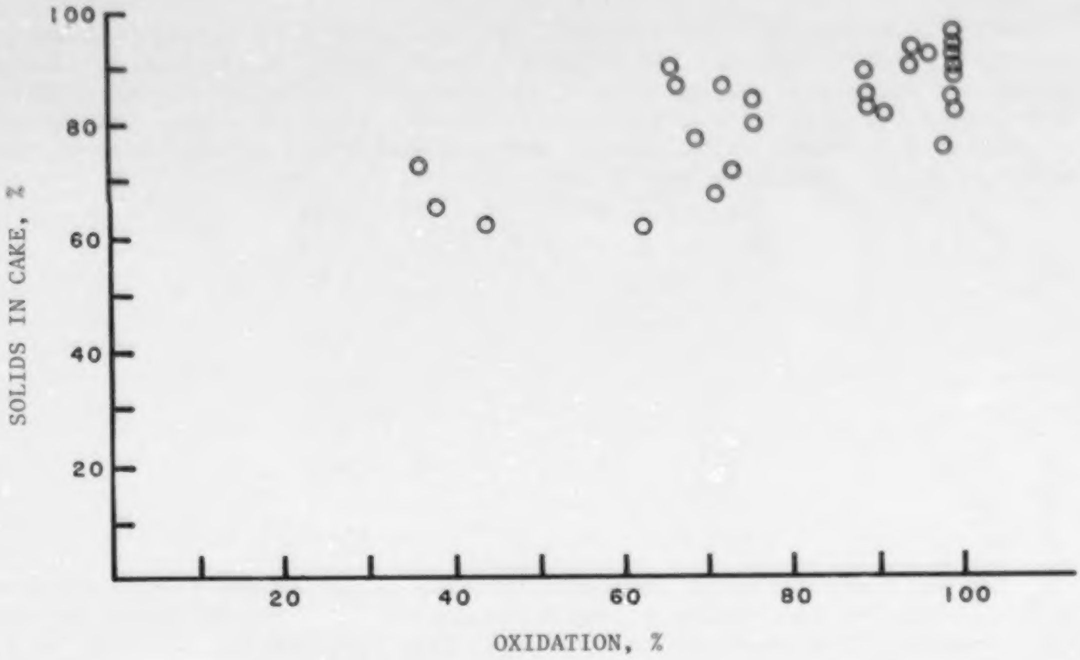


Figure S-4. Relationship of rotary filter cake solids to oxidation level.

CONCLUSIONS

Forced oxidation to levels approaching 100% are possible in the Widows Creek unit 8 FGD system by addition of higher power agitators and an air sparging system. Oxidation in both the absorber and venturi hold tanks with a total air stoichiometry of 2 lb atoms O/lb mol SO_2 absorbed, or more, will consistently produce over 95% oxidation to gypsum at the boiler operating conditions prevailing during the test period without affecting SO_2 removal or operational performance.

Oxidation in the venturi hold tank alone at the same, or slightly greater, air stoichiometry less consistently produced oxidation levels above 95%. The venturi hold tank oxidation mode was compromised by a large liquid entrainment from the venturi to the absorber, which increased the venturi tank pH, thus reducing oxidation efficiency. It is possible that gas flow vanes or mist collectors between the venturi and absorber could reduce the carryover, thus improving oxidation efficiency in this mode.

Gypsum relative saturation was near one during most of the tests with oxidation in both hold tanks. This low level is in agreement with data from other forced-oxidation tests and is attributed to the presence of abundant seed crystals. Forced oxidation should not affect scaling since gypsum supersaturation levels of 1.3 to 1.4 are normally necessary to initiate rapid nucleation that causes scaling.

The tests did not provide data on the effect of increased dissolved solids in the absorbent liquid due to the improved dewatering because only a small portion of the total waste produced was dewatered.

The thickener and rotary filter were oversized for the dewatering characteristics of the waste slurry at oxidation levels over about 90%. The system was operated too far below capacity to provide definitive design and scale-up data. At oxidation levels above 95% the system consistently produced waste solids above 80%. At oxidation levels approaching 100% waste solids approaching 90% were attained. Wastes over about 80% solids were easily handled as a stable solid material.

The crystal size of the highly oxidized waste was primarily in the 20 to 100 micrometer range, whereas the crystal size of the waste produced without forced oxidation is primarily below 20 micrometers.

Laboratory tests of the oxidized waste indicate that the free settling rate of the waste increased little until about 90% oxidation was reached and that it then increased rapidly as the oxidation level increased from 90% to 100%. Above a 95% oxidation level laboratory settling rates were usually 20 to 30 ft/hr. Laboratory filtration tests produced results similar to the rotary filter results. Based on the laboratory tests, the thickener requirements are a minimum 1.7 ft^2/ton-day and the filter requirements are about 200 lb/ft^2-hr.

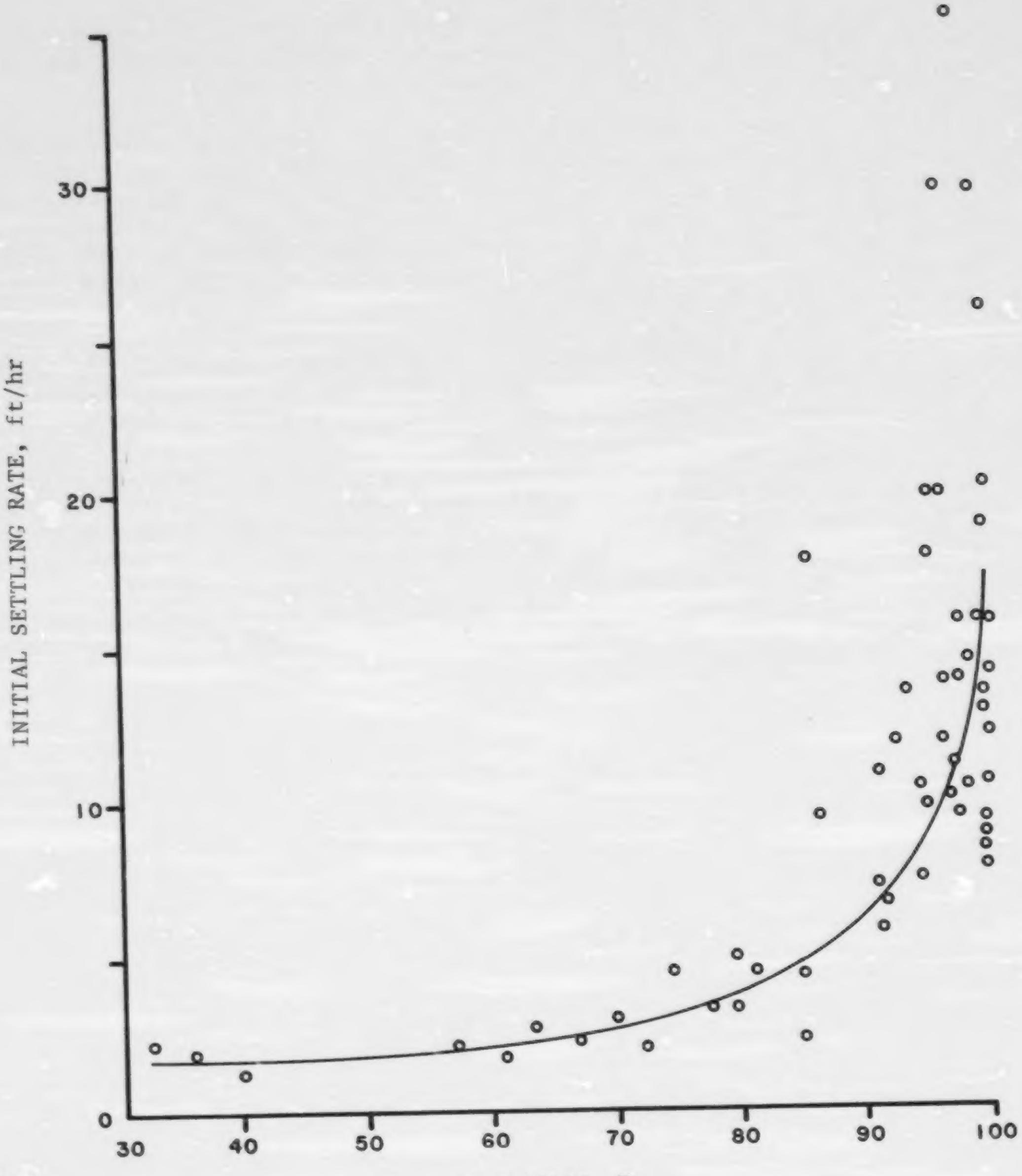


Figure S-5. Settling rate as a function of oxidation level.

FORCED-OXIDATION DEMONSTRATION AT THE TVA WIDOWS CREEK UNIT 8 FGD SYSTEM

INTRODUCTION

In the early 1970's TVA began studies leading to installation of a full-scale limestone scrubbing FGD system on unit 8 of the Widows Creek Steam Plant situated on the Tennessee River near Stevenson, Alabama. Unit 8, a 550-MW boiler which became operational in 1964, is the newest of eight coal-fired units at Widows Creek. With its sister unit, unit 7, it occupies a separate powerhouse about a quarter of a mile from the powerhouse containing units 1 through 6, which have an aggregate capacity of about 850 MW.

The design of the FGD system for unit 8 was based in part on pilot-plant FGD studies. The origins of this design and the pilot-plant studies have been described (1). The system was intended to serve as a demonstration system that would provide design and operating data to improve SO_2 removal efficiency and reliability, which could be applied both to the unit 8 system and to possible future systems. At the time the salient features of the design were completed, ponding appeared the most feasible waste disposal method. A 100-acre, 4.5-million-cubic-yard impoundment was constructed adjacent to an existing ash pond. The pond was estimated to have a capacity equivalent to about seven years of operation. A larger pond was not considered to be justified because of the developmental nature of the project and the possibility that improved waste disposal methods would evolve by the time additional disposal capacity was needed.

The FGD system was completed in 1977. Although many difficulties, by then typical of the early years of FGD system operation, were encountered, the system has operated successfully and has fulfilled the objectives of its installation. Operation of the system in 1977 and 1978 has been described (2,3,4). In addition, TVA is preparing comprehensive studies of various phases of the FGD system performance and waste disposal effects.

In addition to its role as a developmental system, the unit 8 FGD system has also been incorporated into the overall TVA SO_2 emission control plans. As part of a TVA-wide compliance program approved in 1978, the Widows Creek Steam Plant was to meet a plantwide emission limitation of 1.2 lb of SO_2 per million Btu's of heat input by 1981 (5). The program incorporates the use of low-sulfur coal in units 1 through 6, the use of the existing unit 8 FGD system, and installation of a similar system on unit 7. The emission limitation requires a maximum SO_2 emission of 0.9 lb of SO_2 per million

Btu's of heat input (on a 24-hour average) on units 7 and 8. This required an increase in the unit 8 FGD system SO_2 removal efficiency from the original design efficiency of 80%.

Because of the increased quantity of waste that would result from implementation of these plans, it is estimated that existing pond capacity will be exhausted by the end of 1984, adding new impetus to the development of an alternate disposal method. Various landfill methods involving dewatering, stabilization, and fixation of the high-sulfite sludge produced by the unit 8 FGD system and the planned unit 7 system were already being studied by TVA (6). Primary among these studies was the use of dry fly ash for stabilization of dewatered sludge, a method already in widespread use (7). This did not appear possible for the Widows Creek situation because there was insufficient dry fly ash available. Both the unit 8 FGD system and the planned unit 7 system are designed as secondary particulate removal systems. More than 50% of the fly ash is removed in the unit 8 FGD system and about 20% to 30% of the fly ash is removed in the unit 7 FGD system.

Modification of the FGD systems to permit forced oxidation to gypsum was also considered as a method of producing a waste suitable for landfill. By the late 1970's, a substantial body of information had accumulated on limestone forced-oxidation FGD systems, and the dewatering and physical characteristics of the product. For example, extensive studies had been conducted at the EPA-sponsored Shawnee test facility, operated for EPA by TVA at the TVA Shawnee Steam Plant. However, because the Shawnee facility is small (10-MW equivalent) and had been tested at conditions somewhat different from those occurring at Widows Creek, application of the Shawnee results to the modification of a full-scale existing system was considered unlikely to produce an optimum design. Therefore TVA contracted with Combustion Engineering, Inc., to install and operate a full-scale prototype forced-oxidation and a pilot-scale dewatering system for separate testing on the solids on the unit 8 FGD system. As the project would provide additional information for their already extensive studies in limestone forced-oxidation FGD, EPA provided partial funding for the evaluation and publication of the results. Tests were also conducted at the Shawnee test facility using TVA funds.

The forced-oxidation system, consisting of air sparging equipment, was installed on one of the four absorber trains of the unit 8 FGD system. A thickener and rotary filter dewatering system was installed to process about 10% of the absorber waste stream. The objective of the program was to produce a waste composed of 95% oxidation, so that the waste could be dewatered to 80% or more solids. The waste was initially to be reslurried and combined with the remaining FGD waste; later in the program, the waste was to be used in a prototype landfill disposal evaluation.

The demonstration program began in April 1979 and continued until January 1980. Until June 1979 the program was conducted by the C-E Environmental Systems Division of Combustion Engineering with Radian Corporation providing sampling and analytical support. After June 1979 the program was conducted by Radian. The original test plan (8) specified two phases, first an evaluation of three oxidation schemes (absorber hold tank, venturi hold tank, and both hold tanks) followed by optimization studies of the most promising method and initiation of the landfill study. The program was subject to several constraints which limited the extent to which conditions could be controlled and varied for experimental purposes. Flue gas rates varied with the demands on unit 8, which is a cycling or load-following unit, as well as with changes induced by routine maintenance. In addition, the FGD system was operated to meet emission control requirements that could not always be reconciled with test requirements. The unit 8 boiler during the test period was also approaching a mechanical condition that eventually required shutdown for an extensive overhaul. A greater-than-normal number of boiler outages were characteristic of the test program. Since a day or more was necessary to establish steady-state conditions for a test, these factors limited the number of tests conducted and restricted the range of operating conditions that could be evaluated.

This report discusses the background of limestone forced-oxidation FGD as it pertains to the unit 8 demonstration program and presents the results of the test program. Portions, including all of the numerical data, were provided in an unpublished report to TVA by the C-E Environmental Systems Division of Combustion Engineering (9), in published literature (10), and in an unpublished report to TVA by Radian (11). The discussion is limited to the forced-oxidation and dewatering demonstration; the landfill study begun during the latter stages of the demonstration is continuing and is to be reported in the future.

POWER PLANT AND EQUIPMENT DESCRIPTION

The Widows Creek Steam Plant unit 8 and the unit 8 FGD system have been described in the references cited below as well as in those previously cited (1,2,4,5). A site plan is shown in Figure 1. A detailed description of the FGD system is limited to a description of the D train in which the forced-oxidation demonstration tests were performed. The D train is described as modified for the forced-oxidation demonstration test. Except for these modifications, which are identified in the text, the D train description applies to the other three trains. Modifications to the D train itself were limited to installation of larger agitators and air sparger manifolds in the hold tanks. Air compressors and the dewatering system were adjuncts that did not affect the basic FGD system.

BOILER AND FUEL CHARACTERISTICS

Widows Creek unit 8 has a nameplate capacity rating of 550 MW and was put into service in 1964 (12). It is equipped with a Combustion Engineering dry-bottom, tangentially fired double furnace; each furnace has two flue gas ducts. The furnaces were originally pressurized (2) but were converted to balanced draft operation by installation of an ID fan in each of the four flue gas ducts when the FGD system was installed. These ID fans also serve as FD fans for the FGD system. The boiler ESP's remove less than 50% of the fly ash in the flue gas; fly ash constitutes about 80% of the ash in the coal.

The boiler was designed for the use of bituminous coal with a high heating value of 10,500 Btu/lb containing 4% sulfur, 20% ash, and 7% moisture. During the forced-oxidation demonstration test a Kentucky bituminous coal with very similar characteristics was burned. The high heating value was 11,440 to 11,960 Btu/lb, the sulfur content was 3.2% to 4%, the ash content was 11.3% to 16.5%, and the moisture content was 5.3% to 8.2%.

UNIT 8 FGD SYSTEM

The principle design conditions for the unit 8 FGD system were a maximum power unit load of 550 MW; a coal with a 10,000 Btu/lb high heating value containing a maximum of 4.5% (dry basis) sulfur, 25% ash, and 10% moisture; emission of 92% of the sulfur and 80% of the ash in the coal; an excess air rate ot 30%; upstream ESP removal of 50% of the ash in the flue gas; and a maximum limestone stoichiometry of 1.5 mols Ca/mol SO_2 removed using 95% $CaCO_3$, 10% moisture limestone. The FGD system was designed for a maximum particulate emission of 0.06 gr/ft^3 (dry, 1 atm, 60°F) and for 80% SO_2 removal.

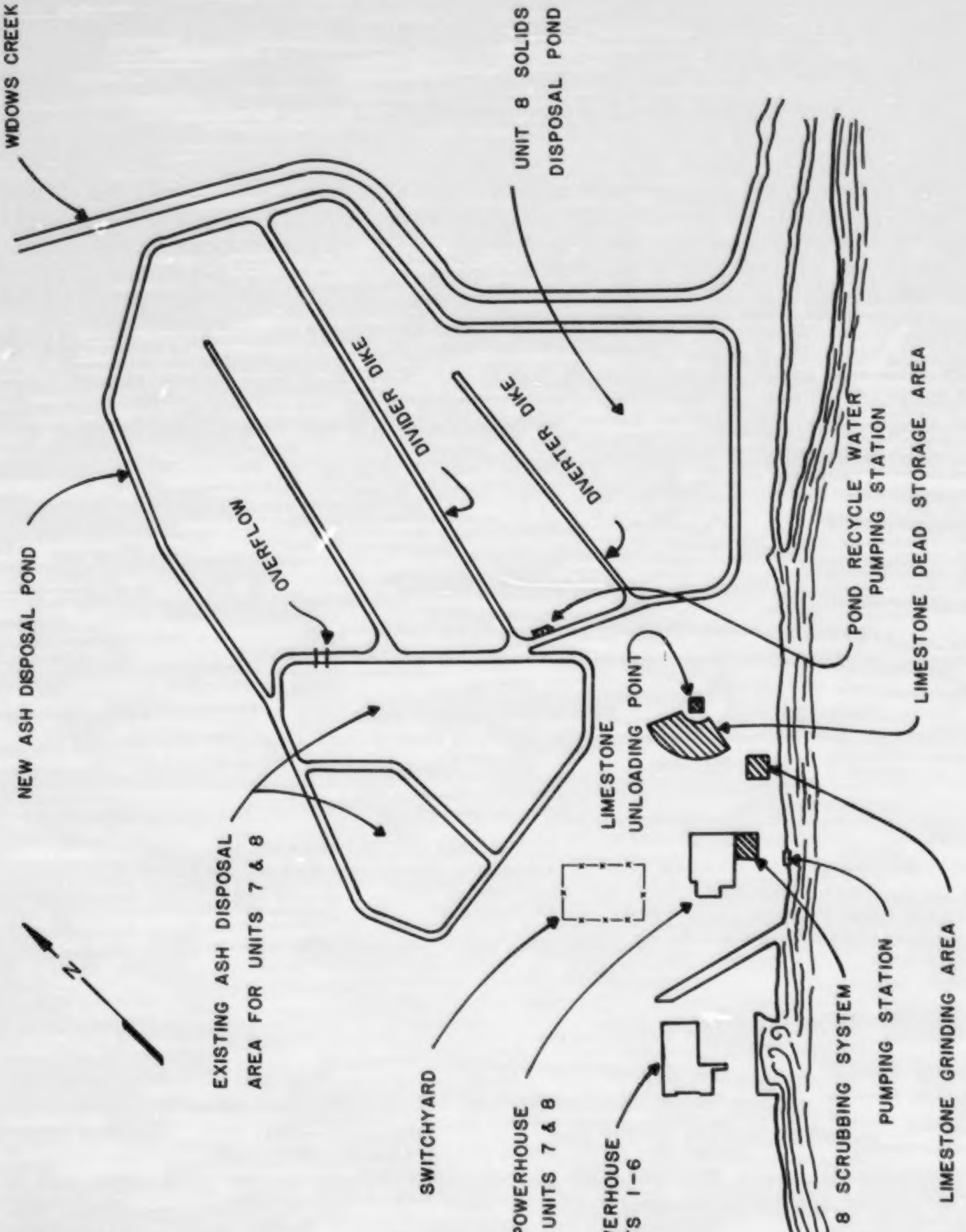

WIDOWS CREEK
UNIT 8 SOLIDS DISPOSAL POND
NEW ASH DISPOSAL POND
DIVIDER DIKE
DIVERTER DIKE
OVERFLOW
POND RECYCLE WATER PUMPING STATION
LIMESTONE DEAD STORAGE AREA
TENNESSEE RIVER
N
EXISTING ASH DISPOSAL AREA FOR UNITS 7 & 8
LIMESTONE UNLOADING POINT
SWITCHYARD
POWERHOUSE UNITS 7 & 8
POWERHOUSE UNITS 1-6
UNIT 8 SCRUBBING SYSTEM
PUMPING STATION
LIMESTONE GRINDING AREA

Figure 1. TVA Widows Creek Steam Plant site plan.

The unit 8 FGD system consists of four identical FGD trains, designated train A, B, C, and D, that scrub all of the flue gas from the boiler. A perspective drawing is shown in Figure 2. One of the trains is connected to each of the four flue gas ducts from the boiler. There is no interconnection between the trains. The boiler ID fan serves as an FD fan for the FGD train; the flue gas ductwork feeding the venturi thus operates under a maximum positive pressure of about 16 inches H_2O.

A single limestone preparation area serves all four FGD trains. Crushed (3/4 inch x 0) locally obtained limestone is dumped to an underground hopper from which it is conveyed to a dead storage area or directly to a 6,400-ton live storage silo. From the silo (which will also serve the unit 7 FGD system) the limestone is conveyed to a wet ball mill in which it is reduced to a 40% solids, 90% to pass 200 mesh slurry. Disposal pond supernate is used for the ball mill water supply.

The effluent slurry normally contains about 10% solids, of which about 25% to 30% is fly ash. Without forced oxidation the sulfur species are about 70% sulfite and 30% sulfate. Four samples during the demonstration test ranged from 18% to 27% sulfate and averaged 22% sulfate, relative to total sulfur species (9).

TRAIN D

The FGD train consists of a venturi - spray tower absorber combination with separate agitated hold tanks as shown schematically in Figure 3. It is described as modified for the forced-oxidation tests. A list of equipment installed for these tests is shown in Appendix A. Flue gas from the boiler ID fan passes downward through the venturi, through the chamber connecting the venturi and spray tower, then upward through the spray tower. The flue gas then passes through a vertical mist eliminator and into a chamber where it is heated to 175°F by mixing it with heated air and vented to the stack.

Slurry is recirculated through the venturi and absorber from their respective hold tanks. Fresh limestone slurry is added to the absorber hold tank. The absorber hold tank overflows to the venturi hold tank, which overflows to the effluent tank from which it is pumped to the pond.

The venturi has a rectangular throat 23 feet long with an effective width of 28 inches in two 14-inch sections. It is designed for a pressure drop of 5 inches H_2O although it often operates at higher pressure drops at reduced loads. The normal slurry recirculation rate is 3,400 gal/min through one pump, providing an L/G ratio of about 8.4 gal/kft^3 at the 405,000 aft^3/min at 280°F flue gas rate used as the forced-oxidation demonstration test datum.

The venturi hold tank, shown in Figure 4, has a diameter of 18 feet, is 25 feet high, and has a capacity of 40,700 gallons. It was equipped with a constant-speed, 75-horsepower, turbine-blade agitator that originally operated at 45 rpm, later increased to 56 rpm. This replaced a smaller existing agitator. The retention time is 12 minutes based on recirculation and 89

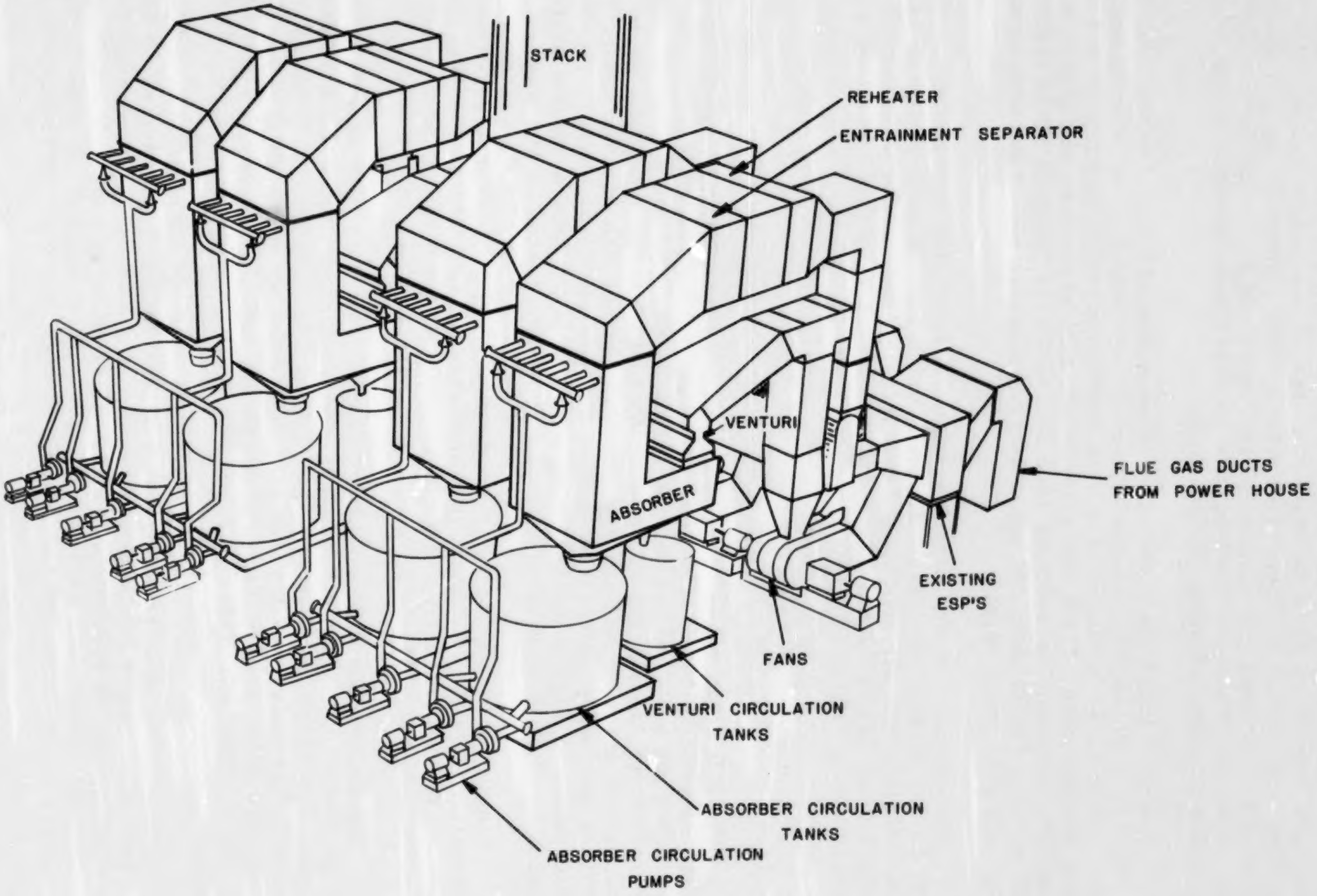

STACK
REHEATER
ENTRAINMENT SEPARATOR
VENTURI
FLUE GAS DUCTS FROM POWER HOUSE
ABSORBER
EXISTING ESP'S
FANS
VENTURI CIRCULATION TANKS
ABSORBER CIRCULATION TANKS
ABSORBER CIRCULATION PUMPS

Figure 2. Widows Creek Unit 8 scrubber area.

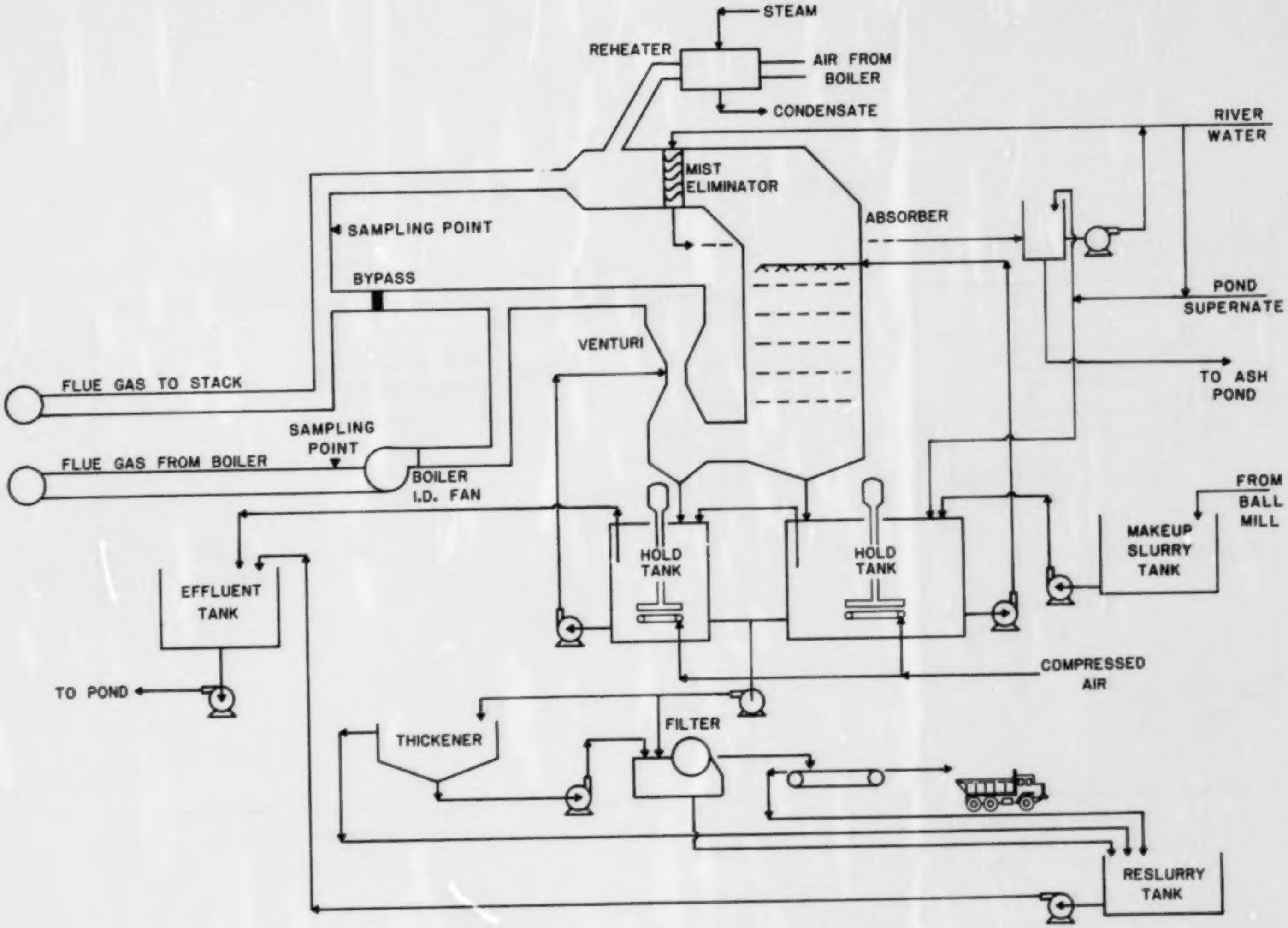
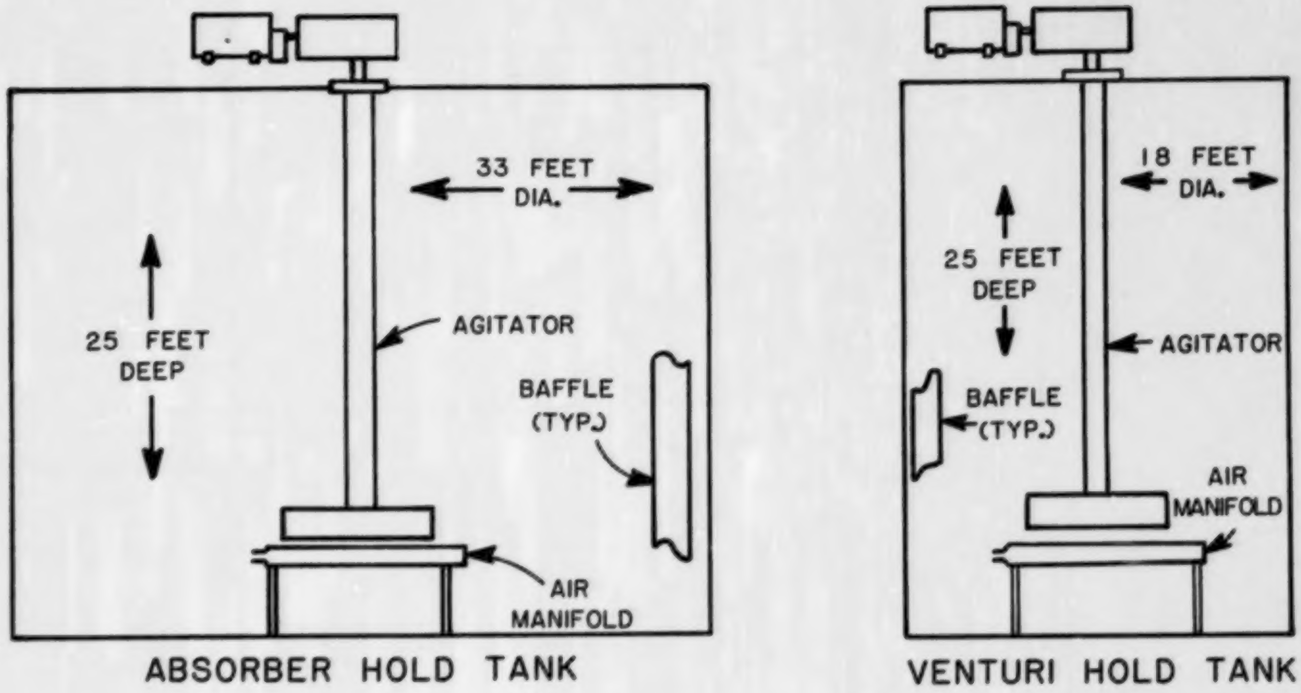

STEAM
REHEATER
AIR FROM BOILER
CONDENSATE
RIVER WATER
MIST ELIMINATOR
SAMPLING POINT
ABSORBER
BYPASS
POND SUPERNATE
VENTURI
FLUE GAS TO STACK
TO ASH POND
SAMPLING POINT
FLUE GAS FROM BOILER
BOILER I.D. FAN
FROM BALL MILL
MAKEUP SLURRY TANK
HOLD TANK
HOLD TANK
EFFLUENT TANK
COMPRESSED AIR
TO POND
FILTER
THICKENER
RESLURRY TANK

Figure 3. Widows Creek unit 8 D-train FGD system flow diagram as modified for forced oxidation.


33 FEET DIA.
25 FEET DEEP
AGITATOR
BAFFLE (TYP.)
AIR MANIFOLD
18 FEET DIA.
25 FEET DEEP
AGITATOR
BAFFLE (TYP.)
AIR MANIFOLD

ABSORBER HOLD TANK

VENTURI HOLD TANK

Figure 4. Absorber and venturi hold tanks.

minutes based on design effluent flow rate. The venturi is designed to reduce the approximately 6 gr/sft^3 of fly ash in the flue gas to a maximum of 0.06 gr/sft^3. It also removes about 15% of the SO_2 in the flue gas.

The absorber is 30 feet by 16 feet in cross section and 34 feet high. The absorber contains five levels of multigrids, primarily intended to improve flue gas distribution and gas-liquid contact. The top three trays are 316 stainless steel to minimize spray erosion and the bottom two trays are fiber-reinforced plastic. An array of low-pressure (Δ5 psi) nozzles distributes the absorbent above the top tray. With clean grids the pressure drop in the absorber is 3 to 4 inches H_2O. The design removal efficiency is about 70%. The normal slurry recirculation rate is 20,000 gal/min, through two pumps, corresponding to an L/G ratio of 49 gal/kft^3 at the 405,000 aft^3/min at 280°F flue gas rate used as the forced-oxidation demonstration test datum.

The absorber hold tank, shown in Figure 4, has a diameter of 33 feet, is 25 feet high, and has a capacity of 150,400 gallons. It was equipped with a constant-speed, 6-blade, 300-horsepower, 68-rpm, Lightnin turbine agitator. The agitator was installed for the forced-oxidation demonstration test, replacing a smaller existing agitator. The retention time in the hold tank is 7 minutes, based on recirculation rate, and 280 minutes based on the design effluent rate.

Although the venturi and absorber have separate hold tanks with series flow of absorbent from the absorber tank to the venturi tank, there is believed to be a considerable carryover of entrained absorbent from the venturi to the absorber. The carryover would increase the flow of absorbent from the absorber tank to the venturi tank and reduce the differentiation of chemical properties of the absorbent in the two recirculation loops. In particular, the lower pH in the venturi, which favors oxidation, could not be attained to the full extent.

Radian (9, appendix B) determined the ash content of the absorber tank effluent as a means of estimating carryover. They assumed all fly ash was removed from the flue gas in the venturi and was thus carried over to the absorber in the liquid phase. In four determinations over about a month the venturi and absorber tanks had the following ash content, representing the carryover shown.

	Ash, g/L		Estimated
Date	Venturi	Absorber	carryover, gal/min
5/7	29	25	1,300
5/17	62	54	1,400
6/11	33	28	1,100
6/18	31	23	600

The average carryover rate of 1,100 gal/min is thus over twice the design effluent flow rate from the absorber to the venturi. About two-thirds of the absorbent flowing from the absorber tank to the venturi tank represents carryover.

OXIDATION

Oxidation air was introduced to the hold tanks through annular manifolds of 12-inch pipe containing holes around the outer circumference. The oxidation tank manifold design is shown in Figure 5. The manifolds were originally mounted directly beneath the agitator turbines. The absorber hold tank agitator was replaced during the tests with one that extended through the manifold.

Compressed air was supplied by 11 Ingersoll-Rand diesel-powered, screw-type compressors with a total capacity of 8,550 ft^3/min at 100 psig. The air was supplied to the manifolds through 2-inch rubber hoses. The flow to each tank was controlled with pinch valves and monitored using a thermometer, pressure gauge, and an orifice plate differential pressure transmitter. Downstream from the pinch valves, water was introduced to saturate the air during operation and flush the lines during shutdown.

The thickener, shown in Figure 6, had a diameter of 20 feet and was 8 feet deep. The scraper blade was driven at about 0.2 rpm. An automatic polyelectrolyte flocculent system was used. Provisions for recycle of the thickener underflow was provided to permit control of underflow solids content.

The vacuum filter, shown in Figure 7, contained a drum 4-1/2 feet in diameter and 6 feet long divided into 12 compartments. The filter cloth was Dacron. The drum operated with 30% to 40% of the circumference submerged in an agitated vat. One-fourth of the filter surface was blocked with shellac because the filter was oversized. The filter cake, normally 1/4 to 1-1/4 inches thick, was removed by reverse air flow and a scraper blade. It fell to a conveyor belt which conveyed it either to the reslurring tank or (by reversing direction) to a truck.

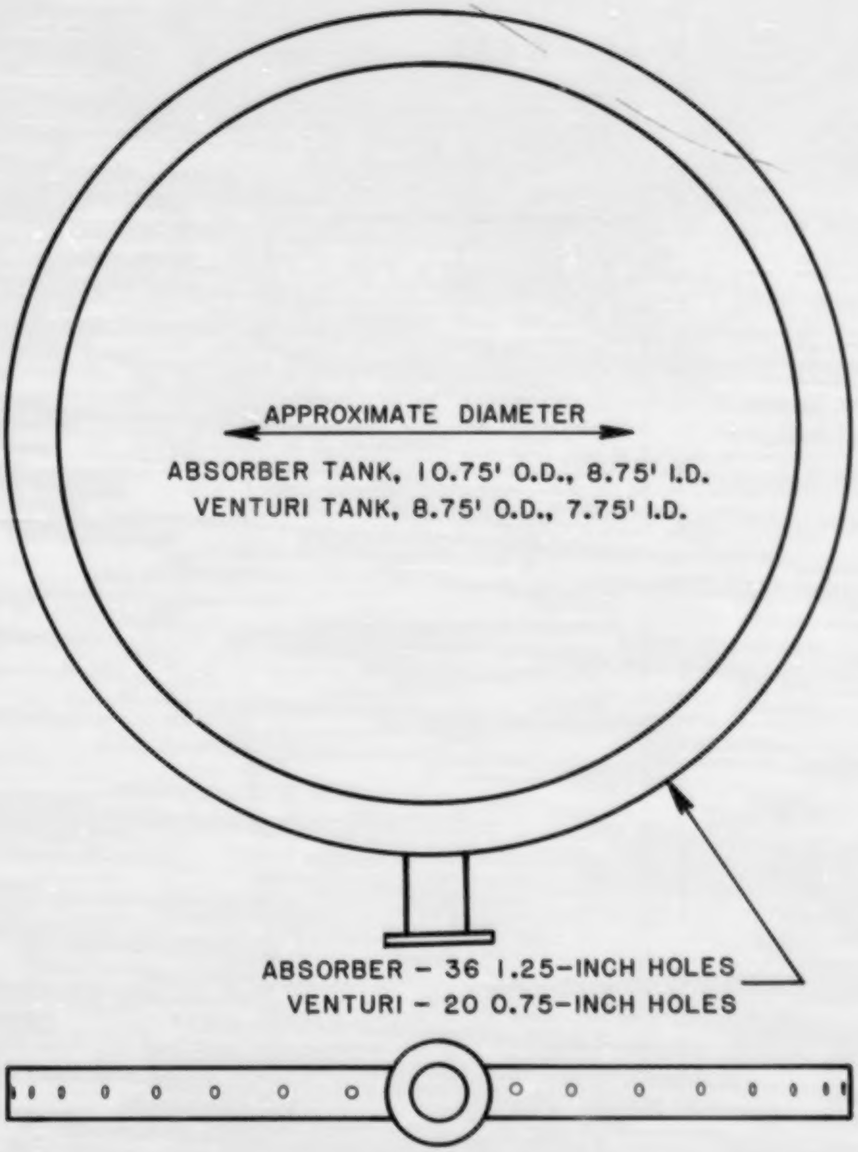

APPROXIMATE DIAMETER
ABSORBER TANK, 10.75' O.D., 8.75' I.D.
VENTURI TANK, 8.75' O.D., 7.75' I.D.
ABSORBER - 36 1.25-INCH HOLES
VENTURI - 20 0.75-INCH HOLES

Figure 5. Air sparging manifold.

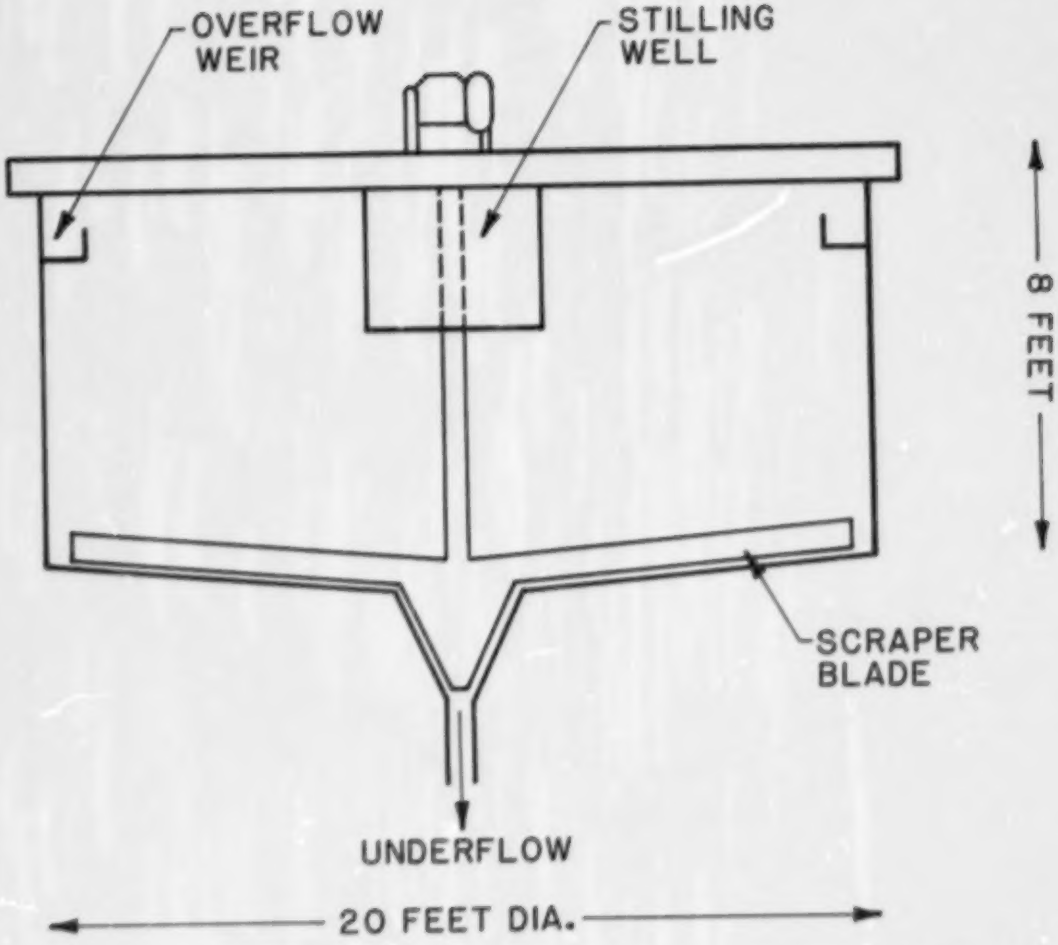

OVERFLOW WEIR
STILLING WELL
8 FEET
SCRAPER BLADE
UNDERFLOW
20 FEET DIA.

Figure 6. Thickener.

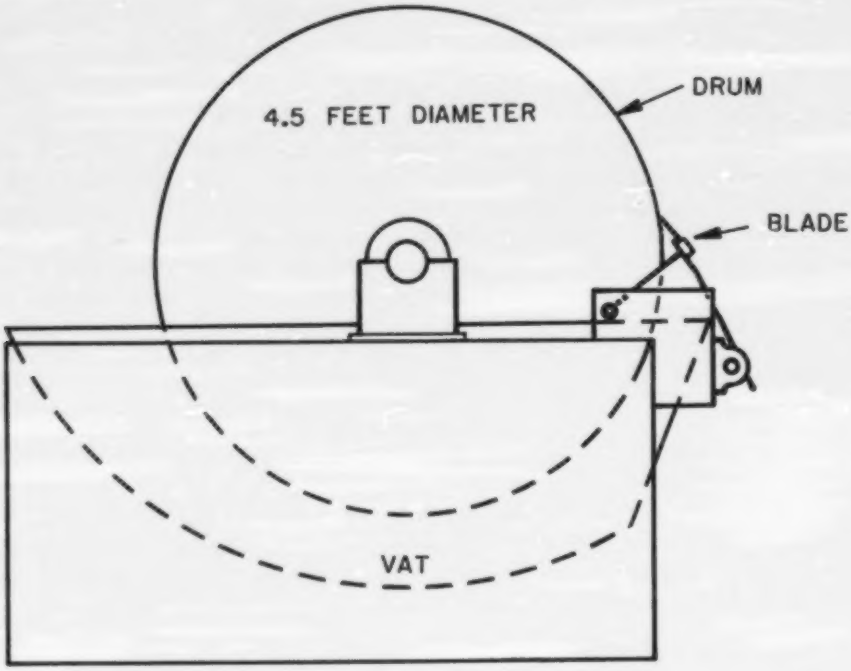

DRUM
4.5 FEET DIAMETER
BLADE
VAT

Figure 7. Filter.

BACKGROUND

Aspects of forced oxidation in limestone FGD processes with a direct bearing on this study include the chemistry of the process, the chemistry of the oxidation process itself, and the development of FGD systems effectively incorporating successful oxidation schemes. The rationale of forced oxidation to produce gypsum is largely related to producing a more easily dewatered and tractable waste requiring less disposal area but other considerations also enter. Prospects for the sale of gypsum for manufacturing purposes appear to be improving. Reduction of water requirements and water discharge may also have important implications in some cases. The increased recycle of water also has important bearing on the overall chemistry and SO_2 removal of the process.

CHEMISTRY

Discussions of limestone FGD chemistry are pervasive in the literature although often in abbreviated or specialized form. Substantial general treatments are provided by Lowell and others (13), Corbett and others (14), Rochelle (15), Head (16), and Slack and Hollinden (17).

Although deceptively simple in abbreviated form, the chemistry of limestone FGD actually involves well over two dozen gaseous, solid, and dissolved species (14,18). Primary among these are gaseous SO_2, CO_2, and O_2; the several hydrated and ionic species of SO_2 and CO_2 in water; and the dissolved and solid species of calcium salts of the SO_2 and CO_2 species. In addition, the effects of other dissolved species, particularly Mg^{2+} and Cl^- must be considered in the chemistry of actual systems. Both invariably enter the system, magnesium from the limestone and chlorides from the flue gas. Although most of the general gas-liquid-solid system operates in a state of considerable disequilibrium, it is convenient from one perspective to regard the chemistry in terms of equilibrium processes. Many design features uniquely important to limestone FGD are, in fact, necessary to allow approach to these equilibria.

In contrast, the chemistry is relatively unencumbered by considerations of pressure and temperature. The pressure is essentially the same for all processes since they operate near atmospheric pressure. The temperature of the liquid is normally about 50°C, the adiabatic saturation temperature of flue gas from utility boilers, which normally leaves the air heater at about 150°C. The effects of such differences in pressure and temperature as exist are seldom discussed in relation to the chemistry of limestone FGD and they are not systematically quantified.

Central to the chemistry from the perspective of equilibrium relationships are the gas-liquid equilibria of SO_2 and CO_2, which in water form the rather complex reaction mixtures commonly called sulfurous acid and carbonic acid. These species provide the basic anions that enhance SO_2 absorption. Neither actually reaches bulk gas-liquid equilibrium and absorption of CO_2, though abundant in the flue gas, is not regarded as an important factor in SO_2 removal (15). CO_2 is actually evolved to the flue gas from dissolution of $CaCO_3$ in many processes (16). The overall equilibria do serve to define the solution chemistry, however.

SO_2 is a readily soluble gas compared with most gases present in flue gas (handbook values show it is over 1,000 times as soluble as O_2 and 50 times as soluble as CO_2, for example), making a high degree of removal at the dilute concentrations found in boiler flue gas practical for absorption processes. The gas-liquid equilibrium relationships for gaseous SO_2 and the solution known as sulfurous acid is

$$SO_2(g) \rightleftarrows SO_2{\cdot}H_2O\ (aq) \qquad H \approx 0.03 \qquad -1-$$

$$SO_2{\cdot}H_2O\ (aq) + H_2O \rightleftarrows HSO_3^- + H_3O^+ \qquad K_1 \approx 10^{-2} \qquad -2-$$

$$HSO_3^- + H_2O \rightleftarrows SO_3^{2-} + H_3O^+ \qquad K_2 \approx 10^{-7} \qquad -3-$$

H is the approximate Henry's Law constant and K_1 and K_2 are the approximate dissociation constants. In pure water the pH equilibrates at about 3 and the $SO_2{\cdot}H_2O$ and HSO_3^- species dominate. The species $SO_2{\cdot}H_2O$ is a loosely hydrated SO2 molecule. It is widely documented (19) that the form H2SO3 does not exist.

The analogous equilibria for CO_2 are

$$CO_2\ (g) \rightleftarrows CO_2{\cdot}H_2O\ (aq) \qquad H \approx 1.2 \qquad -4-$$

$$CO_2{\cdot}H_2O \rightleftarrows H_2CO_3$$

$$H_2CO_3 + H_2O \rightleftarrows HCO_3^- + H_3O^+ \qquad K_1 \approx 10^{-7} \qquad -5-$$

$$HCO_3^- + H_2O \rightleftarrows CO_3^{2-} + H_3O^+ \qquad K_2 \approx 10^{-11} \qquad -6-$$

The chemistry is somewhat more complicated than that of SO_2. H_2CO_3 is a real species although most undissociated CO_2 is loosely hydrated and K_1 represents an "overall" constant considerably smaller than the "true" constant of about 10^{-4} for H_2CO_3 (20). Also, the rate at which CO_2 comes into equilibrium with H_2CO_3 is slow, requiring up to several seconds.

The equilibrium concentrations of dissolved SO_2 and CO_2 and their dissociation products are shown in Figure 8 as a function of pH. Within the pH range normal for limestone FGD, about 4 to 7, the functional species are HSO_3^- and HCO_3^-. Also significant are the pK_a's for equation -3- and equation -5-

dissociations, which fall in the pH range of limestone FGD. The solution is a buffer tending to dampen pH changes and reduce the effectiveness of pH as a control measurement.

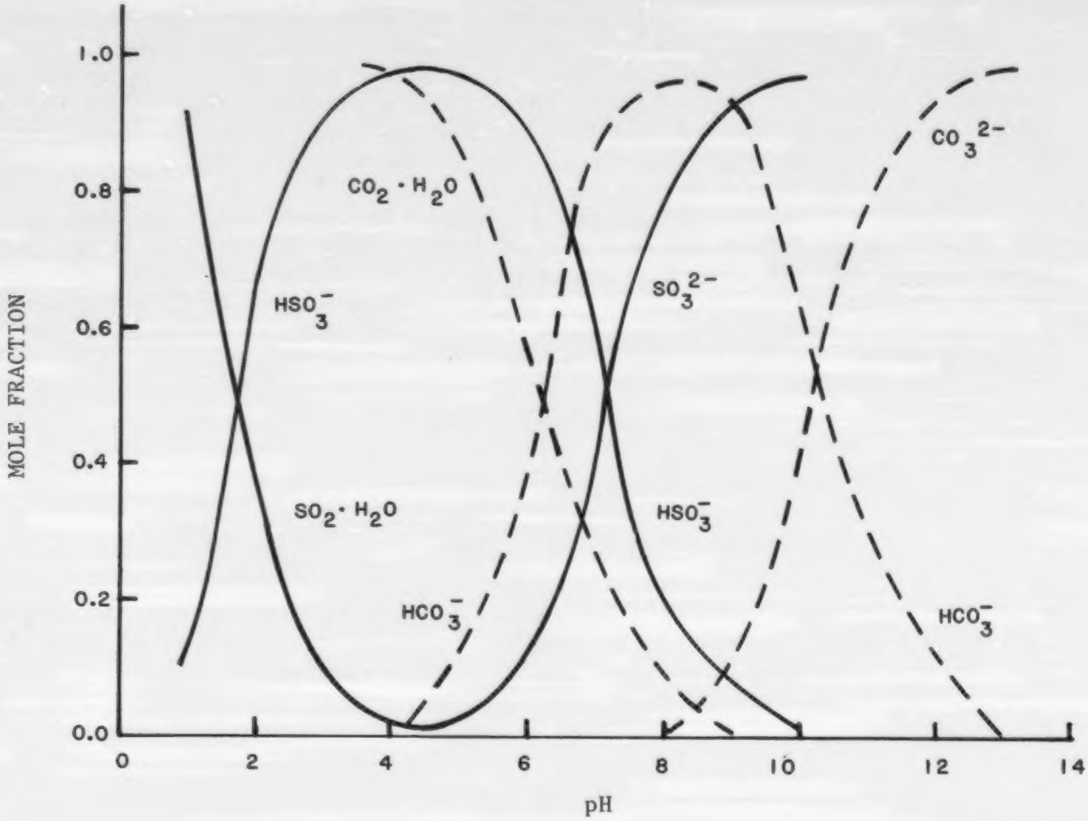


Figure 8. Sulfite and carbonate species as a function of pH.

All of the carbonate species as well as SO_3^{2-}, and of course water, act as Lewis bases to $SO_2 \cdot H_2O$. In a general sense, the liquid phase of limestone FGD chemistry is represented by the reactions of these species. Absorbent, introduced to the absorber at a pH of about 6, absorbs SO_2, which in its undissociated form is acidic, in the Lewis acid - Lewis base sense, to the carbonate species and SO_3^{2-}. The net result is a number of proton exchange reactions that produce, along with a concomitant decrease in pH, HSO_3^- and CO_2. Typical overall reactions of major species are:

$$SO_2 \cdot H_2O + H_2O \rightleftarrows HSO_3^- + H_3O^+ \qquad -7-$$

$$SO_2 \cdot H_2O + HCO_3^- \rightleftarrows HSO_3^- + H_2O + CO_2 \qquad -8-$$

$$SO_2 \cdot H_2O + SO_3^{2-} \rightleftarrows 2HSO_3^- \qquad -9-$$

In actual systems there are a number of additional ionic and neutral dissolved species that also serve as Lewis bases, thus contributing to the alkalinity of the liquid, often significantly. The term total dissolved alkalinity is used to define the concentration of all species that react to form HSO_3^-. Among these are complexes and ion pairs such as $CaOH^+$, $CaCO_3^\circ$, $CaSO_3^\circ$, and $CaHCO_3^+$ (14). Similar species of other cations also contribute dissolved alkalinity.

The result of these rapid ionic reactions is to consume undissociated $SO_2 \cdot H_2O$ and maintain a driving force for SO_2 absorption, without which effective SO_2 removal at practical liquid to gas ratios would be impossible:

$$SO_2\ (g) \rightleftarrows SO_2 \cdot H_2O \qquad \text{-10-}$$

$$SO_2 \cdot H_2O + A^{n-} \rightleftarrows HSO_3^- + AH^{(n-1)-} \qquad \text{-11-}$$

where A is any neutral or anionic species that is a Lewis base to $SO_2 \cdot H_2O$.

A limiting factor in limestone FGD is the low solubilities of both the sulfite and carbonate salts of calcium, which restricts both major sources of dissolved alkalinity. The role of other ions in solution that affect these solubilities is thus a matter of particular importance in limestone FGD. In a general equilibrium sense cations forming more soluble salts than calcium tend to increase the anion concentration and suppress the calcium concentration. Similarly, anions forming soluble calcium salts tend to increase the calcium concentration, thus suppressing the anion concentration. $CaSO_4$ is appreciably more soluble than $CaSO_3$, and SO_4^{2-} is such a modulator of dissolved alkalinity. The other species most frequently considered of major importance are magnesium and chlorine. Sodium may also be important (21).

Magnesium in particular is recognized as an important contributor to total alkalinity (22). Ubiquitous to limestone systems, it is also augmented by deliberate addition of MgO in some processes (23,24). Magnesium oxysulfur salts are considerably more soluble than the corresponding calcium salts and thus, in the equilibrium perspective, increase the concentration of active sulfite (as well as inactive sulfate) and carbonate species while suppressing the Ca^{2+} concentration. In addition, a considerable contribution to total alkalinity is made by the ion pair $MgSO_3^\circ$.

Chloride is also an important component in limestone and other calcium-based FGD processes (25). Depending on the chloride salt content of the coal and the quantity of water purged with the waste, chlorides absorbed from the flue gas as HCl may reach concentrations of at least several thousand parts per million in limestone FGD systems. In addition to the serious corrosion problems it causes (26), the chloride suppresses the total dissolved alkalinity of the liquid by introducing the effects of a highly soluble calcium compound. Ca^{2+} concentration is increased, with a corresponding decrease in dissolved oxysulfur and carbonate species. The practical effect has been shown to be equivalent to the effect of magnesium on an equivalency basis; two equivalents of Cl^- suppressing total dissolved alkalinity to the same extent that one equivalent of Mg^{2+} increases it (16). This role of chloride increases in importance as dewatering efficiency increases and less chloride is purged in the waste. Chloride also suppresses pH because the higher Ca^{2+} concentration suppresses CO_3^{2-} and SO_3^{2-} concentrations.

A reaction of fundamental importance is the oxidation of SO_3^{2-} to SO_4^{2-} by O_2 absorbed from the flue gas, the mechanisms of which are discussed in more detail below. The reaction is rapid and is controlled by the rate at which O_2 is absorbed (27). The quantity of SO_2 oxidized is thus largely a function of the ratio of SO_2 concentration to O_2 concentration in the flue gas. Processes in high-sulfur-coal applications (e.g., 2,000 ppm SO_2 in the flue gas) tend to produce low percentages (10% to 25% of the total SO_2 removed) of SO_4^{2-} while those in low-sulfur-coal applications (e.g., 400 ppm SO_2 in the flue gas) may have oxidation rates of 50% to near 100% (15).

All of these reactions are homogeneous, involving only dissolved species, and are usually regarded, with the exception of those involving HCO_3^- (22), as instantaneous. Essentially the reactions occur in the absorber during an effective residence time of less than a second for venturis and up to a few seconds for spray towers. Quantitative treatment requires rather extensive considerations of diffusivity (22) and determinations of ionic activities under the actual conditions of the solution (13).

In contrast to these rapid homogeneous reactions, the addition of solid $CaCO_3$, as the overall source of alkalinity and Ca^{2+}, introduces solid-liquid reactions of widely different rates and introduces several restrictions on the operation of the system caused by plugging and scaling. The reactions involved in $CaCO_3$ dissolution and $CaSO_3 \cdot 1/2H_2O$ and $CaSO_4 \cdot 2H_2O$ precipitation require at least several minutes to approach an acceptable degree of completion (28). Further, sufficient precipitation must take place outside of the absorber to avoid plugging and scaling. A hold tank providing at least several minutes of effective retention time is necessary (29). The dissolution-precipitation reactions are, ideally, functions of the hold tank regimen.

The dissociation of $CaCO_3$ is dependent on the crystal morphology and the degree of grinding (30). It is rapid under conditions of high disequilibrium, as in the absorber, but the approach to equilibrium at low stoichiometries, as defined by pH change, is measured in hours (29). The typical high stoichiometries of limestone processes, ranging from 1.1 to 1.6 mol $CaCO_3$/mol of SO_2 absorbed, are a reflection of the sluggish dissociation of $CaCO_3$.

$CaSO_3 \cdot 1/2H_2O$ and $CaSO_4 \cdot 2H_2O$ crystallize both by nucleation of new crystals and by growth of existing crystals (31). Both species also tend to form supersaturated solutions. In the presence of adequate seed crystals crystal growth is the dominate mechanism. At high levels of supersaturation relatively sudden homogeneous and hetrogeneous nucleation can occur, which in the case of $CaSO_4 \cdot 2H_2O$ (gypsum), leads to scale formation. Because of the severity of scale problems in limestone FGD, gypsum supersaturation and crystallization mechanisms have been widely studied (14, 31,32). Acceptable scale control requires careful control of gypsum supersaturation levels, particularly in the absorber where SO_4^{2-} is formed and Ca^{2+} concentrations may increase by dissolution of $CaSO_3 \cdot 1/2H_2O$ and $CaCO_3$.

Gypsum supersaturations below 1.3 to 1.4 are generally satisfactory from the standpoint of avoiding scaling (15). Since the quantity of O_2 absorbed is independent of the SO_2 absorbed, the quantity of SO_4^{2-} formed in the absorber is not readily controllable. Large increases in supersaturation are avoided by selection of suitable L/G ratios (to avoid high SO_4^{2-} concentration increases) and conditions that limit large increases in Ca^{2+} concentration (limited dissolution of $CaCO_3$ and $CaSO_3 \cdot 1/2H_2O$). Outside of the absorber gypsum saturation can be controlled to some extent by providing sufficient hold tank residence time for gypsum precipitation. In both, however, provision of sufficient seed crystals is essential. A mitigating factor is the phenomenon of coprecipitation of gypsum with $CaSO_3 \cdot 1/2H_2O$ (23). In limestone FGD systems about 20 mole percent of the $CaSO_3 \cdot 1/2H_2O$ crystals consist of $CaSO_4$ (15). In some systems with low oxidation ratios this removes sufficient $CaSO_4$ for subsaturated operation with respect to gypsum (23).

The critical levels of $CaSO_3 \cdot 1/2H_2O$ supersaturation that can occur are not well defined but are three to four times higher than those of gypsum (14). The same methods applicable to $CaSO_4$ supersaturation control are also applicable to $CaSO_3 \cdot 1/2H_2O$ supersaturation. In addition, pH control is an effective method of preventing excessive $CaSO_3 \cdot 1/2H_2O$ precipitation in the absorber (33); i.e., the species in the relationship

$$HSO_3^- \rightleftarrows H_3O^+ + SO_3^{2-} \qquad -12-$$

can shift from one side to the other within limestone FGD pH ranges. By allowing an adequate decrease in pH through the absorber, the increase in total sulfur species consists of HSO_3^- formation.

Too rapid a decrease in pH, however, may result in limestone blinding, a phenomenon in which calcium sulfite precipitates on the limestone particles, effectively isolating them from the liquid. This is postulated to be an effect of a rapid dissociation rate that produces a localized zone around the particles favorable to $CaSO_3 \cdot 1/2H_2O$ precipitation (15).

Absorber conditions must thus be with an operational envelope defined by pH, L/G ratio, solids concentration and composition, and liquid composition to operate successfully. The particular combinations of these conditions are, in turn, determined by removal requirements and design factors. Typical operating envelopes are difficult to define because of the wide variations in design and operational requirements. One of the most extensive bodies of published data consists of the progress reports of the EPA Shawnee test facility on tests between 1974 and 1979 (16,29,33,34,35). These tests included a venturi - spray tower system similar to the Widows Creek unit 8 system. In general, absorber inlet pH's between 5 and 6 and outlet pH's between 4.0 and 5.5 representing stoichiometries between about 1.1 and 1.6 mol $CaCO_3$/mol SO_2 absorbed provided acceptable operating conditions. Hold tank residence times of 5 minutes or more and at least 8% calcium-sulfur salts ($CaSO_3 \cdot 1/2H_2O$ and $CaSO_4 \cdot 2H_2O$) in the recirculating slurry were also necessary.

SULFITE OXIDATION

Oxidation of SO_2 in aqueous solutions is one of the classic chain reactions of chemistry. As such, and because of its many practical implications, it has been the subject of extensive investigation for many years. The chain mechanism, first proposed by Backstrom in the 1930's, is generally regarded to proceed by a long free radical chain involving $SO_3^- \cdot$ and $SO_5^- \cdot$ (36). The reaction can be initiated by a number of metal ions and can be inhibited by a large number of organic and inorganic compounds. Laboratory studies of the uncatalyzed and catalyzed reaction have generated a large body of literature over the last 50 years. Many of these studies have involved uncatalyzed rate studies (37) and catalyzed rate studies (38). The latter are largely related to the determination of interfacial areas in gas-liquid absorption, for which the reaction is particularly suited (39). These studies are usually made at high SO_2 and O_2 concentrations and at pH's unrelated to FGD conditions. Many of these studies, up to the early 1970's, have been summarized by Hudson and others (40) and Hudson (41). Another extensive area of investigation is in the field of atmospheric chemistry in which the oxidation of SO_2 in homogeneous and hetrogeneous aerosol and droplet systems is widely studied (42).

Among catalysts, the metals of the first transition series, particularly iron, cobalt, manganese, and copper have been most widely used and found most effective. Nonmetals such as NO_2 (43) and chlorine (44) are also effective catalysts.

Alcohols have long been recognized as effective inhibitors (45), along with other organic compounds, particularly those bearing hydroxol groups (46). Copper, sometimes used as a catalyst (47), has also exhibited an inhibitory effect (48).

The general effects of catalysts and inhibitors are well established although specific data such as reaction orders have been hindered by the hetrogeneous conditions under which the body of the experimentation has occurred and by questions raised as to the purity of the solutions used. Contaminants in particular have been an important subject for many years (39). Very low levels of impurities, even by laboratory standards, are known to have important catalytic and inhibitory effects (49).

Both catalysts and inhibitors have been considered in FGD applications. Catalysts were applied in early FGD investigations as a means of producing a marketable acid (48,50,51), as well as producing a high-gypsum waste (52). Catalysts such as iron (53) and manganese (54) have been used in commercial double-alkali processes. Inhibitors have also been used as a means of reducing scaling (32). Studies of the effects of both catalysts and organic acid inhibitors have been made under FGD conditions (41). In general, these studies have demonstrated the strong, sometimes nullifying, effect of both catalysts and inhibitors in sulfite oxidation under FGD conditions. In view of the extensive body of literature casting doubt on laboratory studies of considerable precision (39), projection of qualitative effects, except on a gross scale, of either catalysts or inhibitors in FGD systems would appear unlikely. The use of limestone, the extensive areas of both metallic and organic construction materials, and especially the flue gas with abundant (by laboratory standards) organic materials and fly ash provide rich sources of a wide spectrum of both catalysts and inhibitors. In spite of these complexities, highly effective oxidation of sulfite in FGD systems has proven remarkably easy under a wide range of conditions.

FORCED OXIDATION IN FGD SYSTEMS

Forced oxidation (that is, intentional oxidation approaching total oxidation of the sulfur (IV) species) in FGD processes consists of the simple mechanism of sparging air into the absorbent liquid. In most cases, and certainly in current technology, this is accomplished in unpressurized tanks using low pressure air introduced through simple manifolds. Pressurized reactors and mechanical atomizers (55) have also been used and air-liquid eductors have been evaluated (33). Practical operating conditions in terms of oxidation rate and air rate require only sufficient sulfur (IV) species in solution (a low pH) and a sufficiently long bubble path (liquids depths of about 20 feet, sometimes combined with agitation). Effects of bubble density (the number of bubbles per unit volume of air) are not well defined, although some studies suggest that, in the absence of agitation, bubble density is strongly controlled by hydrodynamic forces related to depth (56).

The quantity of air required to achieve the desired degree of oxidation is expressed as a stoichiometric ratio of oxygen to SO_2 absorbed, expressed as lb atoms O/lb mol SO_2 absorbed, with no allowance for oxidation in other parts of the system. Thus an air stoichiometry of 1.0 represents 0.5 lb moles of O_2 injected and 2.6 lb moles of air injected for 1.0 lb mole of SO_2 absorbed. Stoichiometries of about 1.5 to 3.0 are common, depending on liquid depth, agitation, pH, and other factors.

It is generally concluded on theoretical and experimental grounds that oxygen transfer is the limiting factor in oxidation rate, not the oxidation reaction itself. The oxygen transfer rate is dependent on the rapid depletion of dissolved oxygen, however, and therefore on abundant dissolved sulfite. Efficient oxidation thus requires both an effective gas-liquid contact and a low pH to provide sufficient HSO_3^- in solution. The most effective pH range for limestone systems is about 4 to 5 (15) although effective forced oxidation in limestone processes has been achieved at a pH of about 6 (57). Additives such as magnesium that increase the concentration of dissolved sulfites permit efficient oxidation at higher pH's (33).

Since SO_3^{2-} from dissolution of $CaSO_3 \cdot 1/2H_2O$ provides a portion of dissolved alkalinity in limestone FGD, it has been postulated (33) that forced oxidation will have a deleterious effect on SO_2 absorption. To the contrary, forced oxidation proved to have no effect, and in some cases to enhance SO_2 absorption (33). It has been proposed (58) that air sparging strips CO_2 from the liquid, thus enhancing $CaCO_3$ dissolution. It has also been shown (59) on theoretical grounds that the gas-liquid mass transfer rate of SO2 is larger for liquids without dissolved sulfite species. Since most of the sulfite species in the pH range used for forced oxidation is HSO_3^-, low levels of HSO_3^- will enhance SO_2 absorption according to the relationship shown in equation -2-.

Three general methods of adapting forced oxidation to limestone FGD processes are possible.

1. The use of two or more absorbers, each with a separate absorbent liquid circulating system. The absorbent flows from one absorber liquid circulating system to the next, countercurrent to the flue gas. The venturi - spray tower system with separate effluent hold tanks, such as Widows Creek unit 8, is an example of this method. Makeup absorbent is added to the spray tower liquid system. Overflow from the spray tower system supplies the venturi liquid system. This method is sometimes called two-stage oxidation (33), referring to the two absorbent liquid systems since forced oxidation occurs only in the venturi system, as shown in Figure 9.

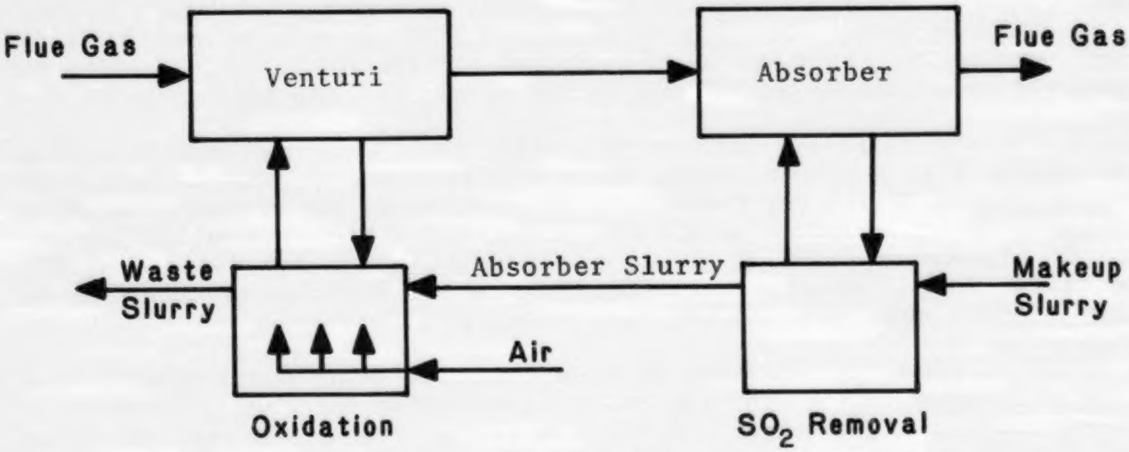


Figure 9. Typical two-absorber forced-oxidation limestone FGD system.

The advantage lies in the pH control possible (33). The absorber can be operated at conditions better suited for efficient SO_2 removal. The venturi can be operated primarily for efficient oxidation at the expense of SO_2 removal efficiency. Spent absorbent from the venturi hold tank absorbs sufficient SO_2 to lower its pH into a range of about 4 to 5, at which oxidation is efficient, without affecting the pH of the absorber hold tank absorbent (35). This oxidation mode is particularly suited for venturi - spray tower systems because the venturi is in any case a relatively inefficient SO_2 absorber.

2. Absorption in a system having a single liquid system, with forced oxidation in the absorbent liquid loop. The system can have more than one absorber in series but only one liquid system so that no difference in properties between the absorbent liquid entering the absorber or absorbers is possible. Systems with a single absorber or a venturi - spray tower system with a single effluent hold tank are examples of this method.

   Oxidation air is sparged into the absorber hold tank while controlling limestone stoichiometry to maintain a sufficiently low absorber effluent pH for effective oxidation. Oxidation efficiencies of over 90% have been attained at absorber hold tank pH's between 5 and 6 and air stoichiometries of 2.0 lb atoms O/lb mol SO_2 absorbed (57). Effective oxidation, however, may require a loss in SO_2 removal efficiency because of pH control limitations. Addition of makeup limestone slurry in a hold tank downstream from the oxidation tank provides increased oxidation and SO_2 removal efficiencies. Additives such as adipic acid may also provide improved oxidation efficiency (15). The attraction of single-stage forced oxidation lies in the more ready modification of existing single-stage systems to forced oxidation and the possibility of less complicated single-stage designs for new systems, a trend seen in current FGD technology (60).

3. Oxidation of the waste bleedstream from the absorber system. Bleedstream forced oxidation consists of oxidizing the absorber effluent waste stream in a separate tank. It has proven impractical in limestone FGD processes because the pH increases, slowing the oxidation rate below practical limits before a sufficient degree of oxidation is attained. This method has required acidification of the slurry or the use of additives such as adipic acid.

The Widows Creek unit 8 system has separate absorbent liquid systems for the venturi and absorber, with flow of absorbent from the absorber liquid system to the venturi liquid system. In this respect it is typical of the method 1 design. The absorbent liquid carryover in the flue gas, described earlier, renders the separation of the two liquid systems incomplete, however. In this respect it resembles a method 2 system. The Widows Creek forced-oxidation demonstration was designed to evaluate both methods, using forced oxidation in either the venturi or absorber effluent hold tank or in both, as discussed in the following section.

Forced oxidation has been a fixture of Japanese double-alkali and proprietary limestone processes for several years (61). These processes have readily produced gypsum suitable for industrial use. In some processes using a low pH absorbent liquid, such as the Dowa process (62), oxidation takes place in the absorber loop. Others such as the Chiyoda 101 (53) and MHI processes (55) incorporate oxidation of the bleedstream using sulfuric acid to maintain a pH of about 4. More recently, commercial in-loop limestone forced-oxidation processes have been developed using absorbers of special design (63,64) or two-stage absorption (65). A number of vendors offer forced-oxidation processes and commercial systems are in operation or being installed at several U.S. utility power plants (66). In at least one case sale of the gypsum produced is anticipated (67).

The most extensive published results of forced-oxidation studies are those obtained by EPA during several years of testing at their Industrial Environmental Research Laboratory at Research Triangle Park, North Carolina, (IERL-RTP) (23) and at the Shawnee test facility (33,57,68), which is operated by TVA. The tests at the Shawnee test facility were conducted in 10-MW mobile-bed absorber (TCA) and venturi - spray tower systems. They consisted of a variety of venturi hold tank, absorber hold tank, and bleedstream oxidation tests. Operating characteristics for oxidation to over 95% gypsum were defined for all three types of forced oxidation. The tests were conducted using coal-fired boiler flue gas containing 2,000 to 3,000 ppm (volume) SO_2 and 3 to 6 $gr/dsft^3$ of fly ash. Tests simulating the anticipated Widows Creek forced oxidation conditions were also made at the Shawnee test facility in early 1979 (69). These are discussed in the test plan and operating conditions section.

The venturi - spray tower system at the Shawnee test facility is generally similar in design concepts to the Widows Creek unit 8 system. It consists (16) of a variable-throat venturi with downward gas flow connecting directly to a spray tower. Normally liquid from the venturi is carried into the bottom of the spray tower with the flue gas and drains into a single hold tank along with the spray tower effluent. For two tank operation a catch funnel with wall baffles in the spray tower above the flue gas inlet collects the spray tower effluent and drains it to the original hold tank. The venturi liquid collects in the bottom of the spray tower and is drained to a separate hold-oxidation tank. There is thus a fairly efficient separation of venturi and spray tower effluent.

The venturi hold tank has an 8-foot diameter and can be operated at 10-, 14-, and 18-foot liquid levels. It contains a 56-rpm, 17-horsepower, 2-turbine agitator pumping downward. The air sparger consists of a 4-foot octagonal of 3-inch pipe with drilled holes directed downward. During the forced-oxidation tests various hole sizes and configurations were used. Injection through single open-ended 3-inch pipe was also used.

The Shawnee system was operated over a wide range of conditions. Oxidation efficiencies of over 95% were attained at oxidation tank pH's of 4.5 to 5.5, oxidation tank liquid depths of 14 feet and above, and air stoichiometries of 1.5 or more lb atoms O/lb mol SO_2 absorbed. The oxidized slurry consistently dewatered to 80% solids or more. Oxidation was equally effective with ringlike air spargers and a single open-ended pipe. Limestone utilization was improved.

The single-tank tests (33) were made with a mobile-bed absorber and may not be applicable to a spray tower system. Acceptable oxidation efficiencies were attained with a single tank for both oxidation and makeup slurry addition although SO_2 removal efficiency was compromised. Improved oxidation efficiency and SO_2 removal efficiencies were attained when a separate, 5-minute hold time oxidation tank was used and the makeup slurry was added to a hold tank downstream from the oxidation tank. Under these conditions 94% oxidation efficiency was attained at an air stoichiometry of 1.7, an oxidation tank pH of 5.5, a liquid depth of 18 feet, and a limestone stoichiometry of 1.3.

OXIDATION TANK DESIGN AND COMPARISON

Several methods have been proposed for introducing air into a tank under conditions which will favor the oxidation reaction. Five methods discussed by Radian (11) are: (1) disc-turbine agitator and sparge ring, (2) draft-tube circulator, (3) predispersion in an external loop, (4) eductor, and (5) air sparging only. The first is the method used at Widows Creek (see Figure 4). The others are shown in Figure 10.

Disc Turbine and Sparge Ring

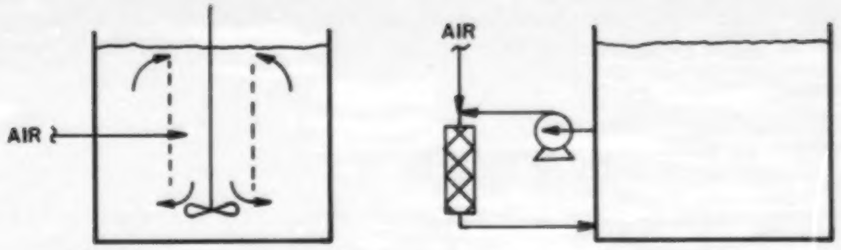
The disc-turbine and sparge ring arrangement is the type of equipment used for the Widows Creek demonstration and a full-scale application would resemble the equipment previously described with one exception. The sparge ring and impeller are normally mounted so that the sparge ring surrounds the impeller just below its horizontal centerline. This enhances the tendency of the radial flow pattern to shear the air bubbles as the air leaves the orifices.

Draft-Tube Circulator

A draft-tube circulator combines a down-draft impeller near the tank bottom with a large-diameter vertical tube mounted concentrically to the impeller shaft, the lower end over the impeller and the upper end below the liquid surface. Air is sparged into the tube about half-way down its length. The air is drawn down the tube and then rises in the tank. The draft tube achieves good mass transfer and provides close control of liquid flow patterns.

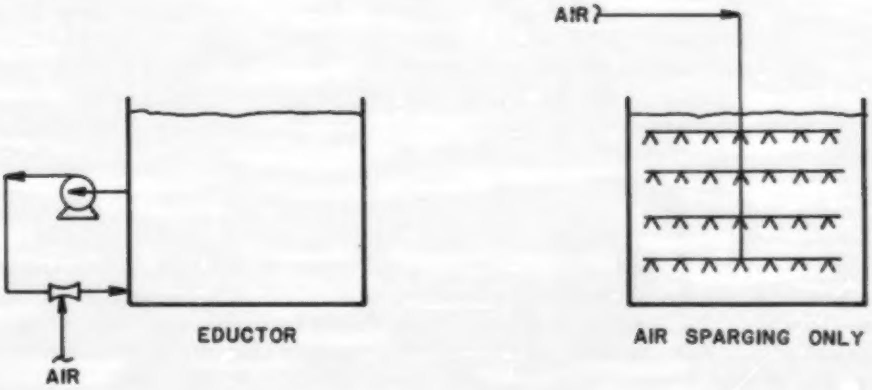
Predispersion in an External Loop

Predispersion in an external loop involves pumping the slurry through a static mixer and back into the tank. The static mixer consists of a pipe containing fixed vanes and baffles, which repeatedly shear and remix the inlet stream. Air introduced upstream from the static mixer is sheared into fine bubbles and evenly dispersed before being introduced into the bottom of the tank. Predispersion is being investigated by a vendor but has not been demonstrated.



DRAFT-TUBE CIRCULATOR

PREDISPERSION (WITH STATIC MIXER)



EDUCTOR

AIR SPARGING ONLY

Figure 10. Oxidation methods.

Eductor

Eductors have been tested in forced-oxidation application at the EPA IERL-RTP and at the Shawnee test facility (35). Slurry is pumped at high velocity through the eductor nozzle. The eductor draws in air at atmospheric pressure. The high velocity in the eductor nozzle serves to shear the air into fine bubbles as it is introduced into the tank bottom. Both the IERL-RTP and the Shawnee tests employed normal or slightly increased agitation levels in the hold tanks.

Air Sparging Without Mechanical Agitation

The forced-oxidation system now under construction at the TVA Paradise Steam Plant will employ a network of pipes to distribute air throughout the hold tank, with only normal agitation and circulation. The vendor has installed a similar system for a western utility, but the design has not been demonstrated with high-sulfur coal (i.e., at high-oxidation rates).

Comparison of Methods

Power consumption is the primary factor affecting the operating costs of a forced-oxidation system since the system consumes only air. The three components that will consume power are the agitators, the air blowers, and, in some systems, the additional slurry pumps. Table 1 presents a rough comparison of the power requirements of the five options described. The table shows that a savings in power in one area generally requires more power in another area. The capital requirements of a system will depend on the capacity and type of equipment necessary. Generally, large power requirements in one area will be reflected by large capital requirements for that area. The table also lists major equipment and a rough comparison of capital requirements for the five methods.

A system based on eductors does not require air compressors, but the power savings are more than offset by increased slurry pumping power since eductors are not energy-efficient pumps. Overall power consumption is high. Capital requirements are fairly low, involving only slurry pumps and eductors. Reliability is questionable, because the eductor internals would be subject to very high slurry velocities and high erosive forces.

Predispersion in an external loop has not been demonstrated as a workable oxidation system, and it is difficult to assess its potential. If the static mixer can produce fine enough bubbles, low air rates may be possible. Hence combined air blower and slurry pump power requirements could be low, but both the air blower and the pump have to overcome the pressure drop and the tank hydrostatic head. Perhaps the biggest question concerning this option is reliability. Plugging, scaling, and erosion are common FGD problems that may have severe effects on static mixer efficiency. Capital requirements could be high, including blowers, pumps, and static mixers.

The air-sparging-only design has not been demonstrated but it is possible to make some assessment of it. Since the design employs only minimal agitation, either high air rates or a high sparger pressure drop must be used

TABLE 1. COMPARISON OF OXIDATION METHODS

System	Agitator power	Blower power	External pump power	Equipment requirements	Capital requirements	Comments
Disc turbine	High	Moderate to high	None	Agitators Blowers Sparge rings	Moderate	Widows Creek Demo Unit
Draft tube	High	Moderate	None	Agitators Draft tubes Blowers Spargers	Moderate to high	Demonstrated
Predispersion in an external loop	Normal	Moderate to high	High	Slurry pumps Blowers Static mixers	High	Not demonstrated - paper study only
Eductor	Normal	None	High (could also use steam)	Slurry pumps Eductors	Moderate	IERL-RTP and Shawnee
Sparging only	Normal	High	None	Blowers Sparge network	Moderate	2 Demo units built or under construction (incl. TVA Paradise Steam Plant)

Source: (11)

to obtain good mass transfer. Either alternative incurs a power cost, and this design will have a blower horsepower requirement much higher than the other alternatives. Capital requirements will be moderate unless the sparger network is very complex. Two factors should be considered to evaluate reliability: settling of solids and plugging of the sparger system. In a system that depends solely on sparging, plugging and scaling in the sparger network are also proportionally more important.

From a technical standpoint, the two most promising systems are the disc turbine - sparge ring and the draft-tube circulator. Two vendors, Chemineer, Inc., and Lightnin Mixing Equipment Company, Inc., indicate that the disc-turbine and sparge ring design could be considered state-of-the-art for most oxidation applications. The design has been used extensively in wastewater treatment, where experience indicates that power should be distributed to the blower and the agitator. The overall power requirements are moderate, and air stoichiometries encountered during testing at Widows Creek are reasonably low. Consequently, operating costs should be moderate.

A draft-tube circulator can achieve better mass-transfer than a disc-turbine - sparge ring arrangement, but capital costs are higher. Southern California Edison, working with Swensen Engineering and Lightnin, successfully demonstrated this type of design for forced oxidation several years ago. However, Lightnin's analysis of the Widows Creek demonstration indicated that adequate results could be obtained using the disc-turbine - sparge ring design, and that the draft tube would not reduce total power consumption enough to justify the additional capital expense. Table 2 shows capital cost estimates developed by Radian (11) for disc-turbine - sparge ring and draft-tube circulator systems and a capital cost estimate for a centrifugal air compressor system.

In summary, the disc-turbine and sparge ring design appears to be the best available. Neither the predispersion design nor an air-sparging-only design has been demonstrated. A design using eductors for sparging will have high power requirements. While a draft-tube circulator would be a slightly better mixing device than the disc turbine - sparge ring, the marginal power savings might not justify the increased capital expense.

WASTE DEWATERING

Almost all of the limestone FGD systems that incorporate mechanical dewatering of the waste stream to produce a solid waste employ a two-stage process consisting of a thickener followed by a rotary vacuum filter. Other mechanical dewatering methods such as hydroclones, mechanical clarifiers, belt and leaf filters, and centrifuges have been evaluated or have found limited use. Extensive discussions of sludge (although not FGD sludge) dewatering equipment and its performance are provided by Knight and others (66), an EPA sludge disposal manual (70), and Wilhelm and others (71).

Projects by EPA and the Electric Power Research Institute (EPRI) have produced a body of open literature that provides a comprehensive view of the

TABLE 2. CAPITAL COST ESTIMATES FOR DISC-TURBINE AND DRAFT-TUBE CIRCULATORS

Vendor	System[a]	Estimate per scrubber train[b]
Chemineer	Disc turbine	
	Absorber tank (125 hp)	\$ 64,600
	Venturi tank (40 hp)	\$ 25,000
Lightnin	Disc turbine	
	Absorber tank (200 hp)	\$ 53,000
	Venturi tank (40 hp)	\$ 30,000
Lightnin	Draft tube (DAT aerator)	
	Absorber tank (200+ hp)	\$107,000
Air Compressor[c]		
Vendor	Ingersoll-Rand	
Compressor type	Electric centrifugal	
Capacity	6,000 ft^3/min	
Outlet pressure	40 psig	
Drive	800 hp	
Estimate	\$112,000 and \$20,000 to \$40,000 for accessories	

[a] Estimates cover motor, gearbox, shaft, impeller, (draft tube), and design of sparge ring for one train. Sparge rings and air compressors are not included.

[b] Estimates obtained by Radian Corporation (11). Costs are 1980 dollars.

[c] Estimate is for skid-mounted motor, drive, compressor, inlet filter, and control panel. Two 6,000 ft^3/min units would be required for unit 8.

field. The EPA program, Control of Waste and Water Pollution from Coal-Fired Power Plants, encompasses a number of programs related to disposal of limestone and lime scrubbing FGD wastes. Results of the program, as well as other related work, have been summarized by The Aerospace Corporation and Arthur D. Little, Inc. (72). Among these studies are field evaluations at the Shawnee test facility (73), and a series of economic evaluations of disposal methods by TVA (74). EPRI has produced an integrated series of studies under their projects RP 786 and RP 1260, among which is the FGD Sludge Disposal Manual (66) dealing with a broad spectrum of FGD waste disposal technology and practices. The project also produced an FGD waste data base (75), a study of chemical and physical properties (76), and a review of sludge dewatering technology (71).

Waste sludges differ widely in dewatering characteristics depending on a number of properties such as the specific crystallization mechanism and the presence of fly ash. A basic difference exists, however, between high sulfite wastes and wastes in which the sulfur is 90% or more gypsum. The small platelet form of $CaSO_3 \cdot 1/2H_2O$ (2 to 10 micrometers) (77) results in slow settling rates and a high degree of water retention under practical dewatering methods. The filtered waste usually contains 30% to 60% water and requires stabilization for landfill disposal. Gypsum consists of larger (50 to 100 micrometer) crystals that produce settling rates several times greater (77) than the sulfite and which can consistently be dewatered to less than 20% water. The dewatered waste appears to be widely regarded as a suitable landfill material without stabilization although no large-scale disposal evaluations of FGD gypsum using true landfill methods have been completed (78).

Thickening and Filtration Technology

Radian (11) has summarized dewatering technology with particular reference to the Widows Creek application. In addition to the technical and theoretical considerations, cost estimates for a thickener and filter system for a full-scale installation are also discussed.

Thickening--

The primary purpose of the thickening step is to increase the 8% to 16% solids waste stream from the FGD system to 30% to 50% solids, a concentration more suitable for a filtration process. Although the dilute slurry could be fed to a vacuum filter directly, the capital cost for a thickener is usually offset by the corresponding decrease in filter area required.

Figure 11 is a typical plot of batch settling test results (11). The variables are defined as follows:

H_o = initial height of interface

C_o = initial solids concentration, mass solids volume

= (initial wt % solids)(density of underflow)

$C_u = C_o (H_o/H_u)$

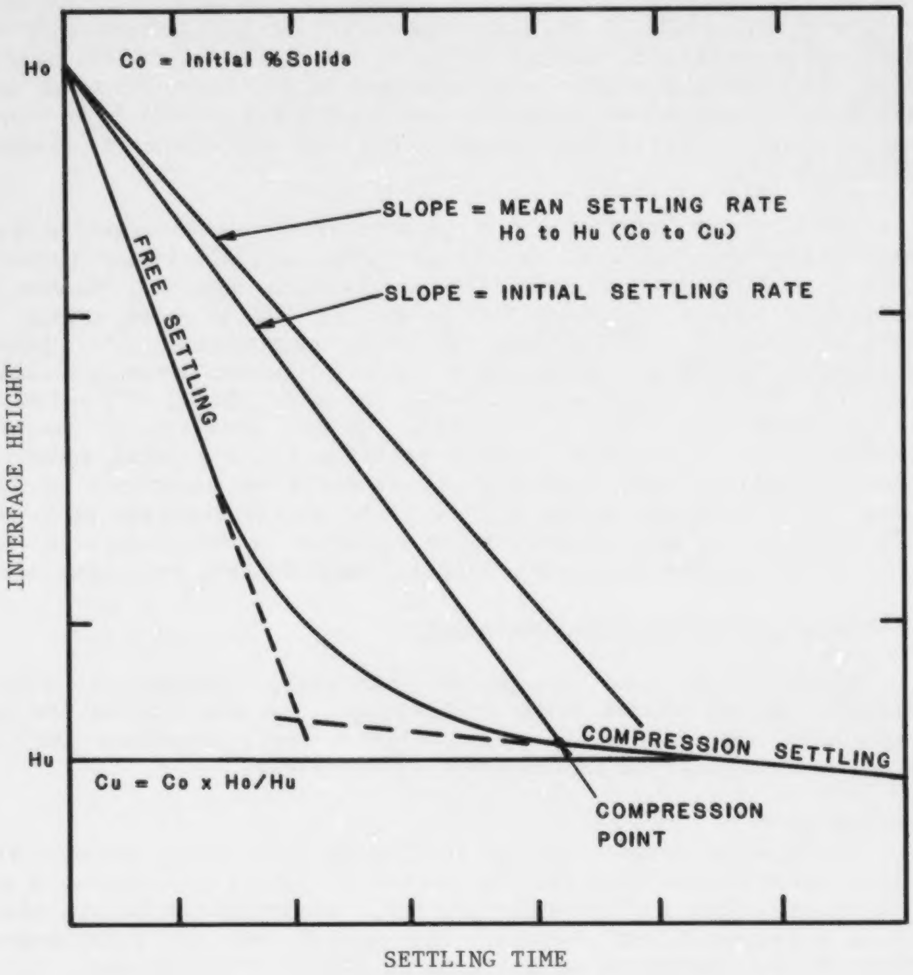


Figure 11. Settling test diagram.

H_u = interface height corresponding to C_u

For any height H_x, C_xH_x = constant

$C_oH_o = C_uH_u$

Initial settling will usually be in the free-settling region, and settling velocity will at first be constant. When the settled pulp reaches a certain density, the proximity of the particles to each other will tend to interfere with settling. This stage is known as compression settling. Figure 12 is a cross section of the settling zones in a typical thickener (in operation). Zones A and B correspond to the free-settling region in Figure 11. Zones C and D correspond to compression settling in Figure 11.

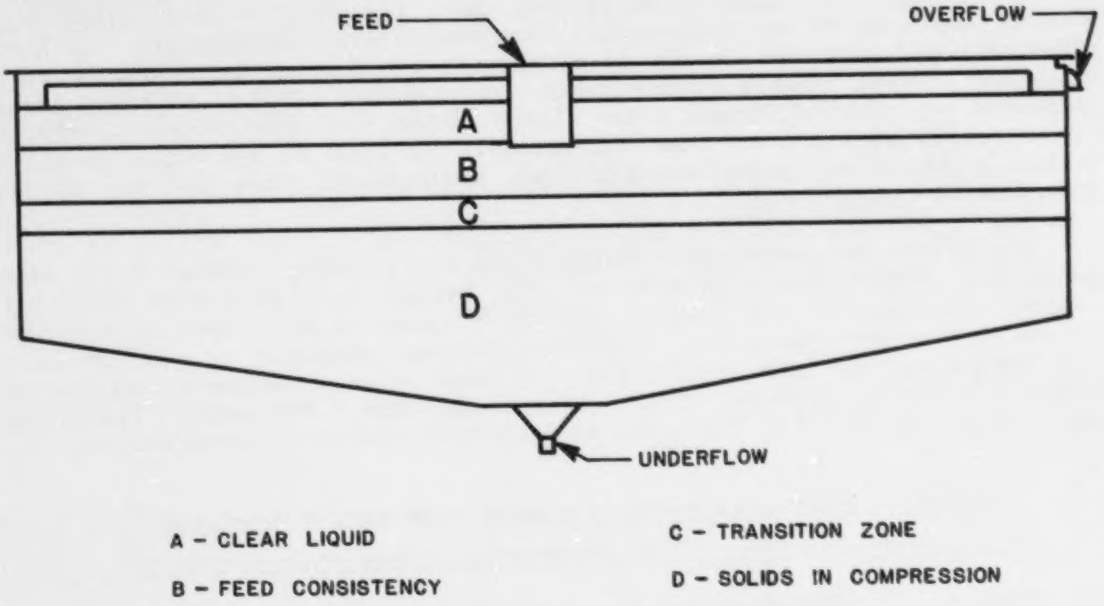


Figure 12. Section of a continuous thickener.

One of two factors controls the sizing of a thickener, the mean settling rate (unit area), or the compression-zone volume. The mean settling rate is calculated from Figure 11 as the slope of a line from the initial height to the height that corresponds to the underflow concentration. This settling rate can be used to calculate the unit-area required for settling, as follows:

Assume 10% solids in feed, 1.06 density, 10 ft/hr settling rate

$$C_o = \frac{0.1 \times 1.06 \times 62.4}{2000} = 3.31 \times 10^{-3} \text{ ton solids/ft}^3$$

$V = 10\ \text{ft/hr} = 240\ \text{ft/day}$

$A = \dfrac{1}{C_oV} = 1.3\ \text{ft}^2/\text{tpd}$

For this example, if unit-area is controlling, 1.3 ft^2 of thickener area must be allowed for each ton per day of solids to be processed. Two vendors, Dorr-Oliver, Inc., and Environmental Elements Corporation, suggest that typical unoxidized FGD sludges will have unit-area requirements of from 5 to 40 ft^2/tpd. Oxidized sludges have mean settling rates many times higher than this, and unit-area requirements of 5 ft^2/tpd or less.

If the feed pulp is to be thickened substantially past the compression point, thickener sizing may be controlled by compression-zone characteristics and not unit area. In this operating region, the residence time of a particle in zones C and D of Figure 12 is so long that the volume of these zones will control the size of the thickener. Compression-zone settling has not been rigorously modeled, and design of thickeners in this region requires more extensive testing than a simple batch settling test (79). Settling tests performed on oxidized Widows Creek sludge showed that the compression-point concentration was greater than 40% solids. It will be possible, then, to design a thickener based on unit-area requirements only if the design underflow is not over 40%.

One of the most expensive subsystems in the thickener system is the rake mechanism. There are a variety of rake designs available from thickener vendors. For any FGD application, both Dorr-Oliver and Environmental Elements recommended a very heavy-duty mechanism with an automatic or semiautomatic lift device on the rake arms. Table 3 shows a rough estimate prepared by Radian (11) for a thickener capable of treating unit 8 FGD waste. The design basis, 2,400 tpd and 5 ft^2/tpd, can be considered extremely conservative.

TABLE 3. COST ESTIMATE FOR A WIDOWS CREEK UNIT 8 THICKENER

Vendor	- Environmental Elements
Throughput	- 2,400 tpd of oxidized sludge
Unit area	- 5 ft^2/tpd
Diameter	- 135 ft
Rake	- 120,000 ft-lb torque, semiautomatic lifting device
Materials	- Carbon steel lined with 1/8 in. neoprene rubber
Estimate	- $150,000 exclusive of tank

Estimate obtained by Radian (11). Costs are 1980 dollars.

Operating expenses for a thickener are usually very low. Although the rake drive requires very high torque, the low speed results in low power consumption. When a flocculent is used, flocculent cost may overshadow power consumption as an operating cost. Reliability of a full-scale thickener can be expected to be very high.

Filtration--

Forced oxidation has two major effects on filtration, an increase in maximum filter loading and an increase in product dryness. Typical unoxidized sludges will dewater to 55% to 65% solids, with design filter loadings of 50 to 60 lb/hr-ft^2 of solids. Oxidized sludges, because of their larger particle size and lower surface-to-volume ratio, will dewater to 80% to 85% solids, with filter loadings from 150 to 250 lb/hr-ft^2 of solids.

There are several different vacuum filter configurations, but the two that are of primary interest in FGD applications are the rotary drum and continuous belt filters. The rotary drum filter used at Widows Creek is described in the power plant and equipment description (see Figure 7). A rotary drum filter uses blowback and a scraper blade to discharge the cake, whereas the continuous belt is drawn out over small diameter discharge rollers and back to the drum surface. The continuous belt mechanism has a higher initial cost, but has several advantages. Because the cloth is not sealed to the drum, it can be changed much more quickly. On the small demonstration unit, it required two men an entire shift to seal a new cloth to the drum of a rotary drum filter. Because there is no scraper blade rubbing on the cloth, cloth wear and blinding are also reduced for the continuous belt filter. And because the cloth is drawn away from the drum, it is possible to wash both sides before the cloth is returned to the slurry. This will also reduce blinding.

One vacuum filter vendor, contacted by Radian (11), recommended a filter loading of about 200 lb solids/hr-ft^2 as a design basis for oxidized Widows Creek waste, based on particle size data. A rough estimate for a full-scale system is presented in Table 4.

TABLE 4. COST ESTIMATE FOR A WIDOWS CREEK UNIT 8 VACUUM FILTER

Vendor	- Komline-Sanderson Engineering Corp.
Area loading	- 150 to 250 lb/hr-ft^2 of solids
Area	- 600 ft^2 (12 ft diameter by 16 ft face)
Capacity	- 1,400 tpd
Blower	- 5 hp centrifugal
Agitator	- 7.5 hp
Drum drive	- 7.5 hp
Receiver	- 48 in. diameter by 84 in. height
Vacuum pump	- 125 hp Nash CL2002
Filtrate pump	- 10 hp centrifugal
Estimate	- $110,000 for carbon steel, $200,000 for 317L stainless steel

Estimate is for filter delivered with receiver, vacuum pump, and filtrate pump skid mounted. Three to four 600 ft^2 units would be required for the combined output of units 7 and 8. Estimate obtained by Radian (11). Costs are in 1980 dollars.

MODELING

Many mathematical models have been developed for various aspects of limestone FGD. Wen and Fan (80) summarize a number of such models dealing with SO_2 absorption and chemical equilibria. Radian developed a chemical equilibrium model that incorporates some two dozen chemical species (13). This model is incorporated in an extensive computer model developed by Bechtel National, Inc., and TVA based on Shawnee test facility data. The model projects full-scale design, operating, and economic data for a variety of limestone and lime FGD systems, including venturi - spray tower forced oxidation processes. It has been discussed in EPA FGD symposium papers (81,82), Shawnee test facility reports (16,33,83), and a users manual (84). Borgwardt discusses a model for forced oxidation in limestone FGD processes in his 1977 publication on sludge oxidation (57). Hudson (41) describes a similar model based on extensive experimental data on catalyzed, uncatalyzed, and inhibited reaction orders, $CaSO_3 \cdot 1/2H_2O$ solubility relationships, and pH effects.

The models for SO_2 removal and forced oxidation are generally based on gas-liquid mass transfer equations for absorption followed by a chemical reaction. Theoretical treatments of film and surface renewal theory from which these equations are developed are discussed by Zenz (85) and Danckwerts (86). No rigorous mathematical treatment for such absorption processes exists and there are several variations of the basic theories (87). In addition, numerous simplifying assumptions, such as chemical equilibrium and use of overall transfer coefficients, are necessary in FGD models because data on absorption and reaction orders are not well defined. The general form of the models usually consists of an equation based on absorption theory expressions which is fitted to actual data by coefficients representing operating conditions found to, or assumed to, affect SO_2 removal. The resulting equation is thus specific to the system in which the data were developed to some extent, although most models are regarded as applying generally to similar systems. Zenz (85) provides an excellent review of the formal methodology and its practical and emphirical treatment.

In the case of forced oxidation in FGD processes there are four general processes that may control the overall oxidation process: (1) the dissolution rate of solid $CaSO_3 \cdot 1/2H_2O$, (2) the oxidation reaction rate, (3) the overall absorption of oxygen, and (4) the precipitation of $CaSO_4 \cdot 2H_2O$. The dissolution rate is obviously a factor at high pH's. At lower pH's, with high levels of HSO_3^- in solution, dissociation is sometimes not regarded as a rate-limiting factor (11). It also will not be a factor in single-stage oxidation if $CaSO_3 \cdot 1/2H_2O$ does not precipitate in the absorber. The oxidation reaction has been extensively studied (39,41,57) and is not regarded as a rate-limiting factor. In most cases oxygen absorption is regarded as rate-limiting under FGD conditions.

Using film theory and substituting overall mass transfer coefficients by standard methods, Combustion Engineering (9) developed an expression for oxidation in forced-oxidation tanks:

$$r_{ox'ht} = (2G_aV_t\ C_{O_2}RT/h_tP_T)\ (1 - \exp(-K_Lah_tP_T/G_aH)) \qquad \text{-13-}$$

where

$r_{ox'ht}$ = oxidation rate, lb-mol/min

G_a = air rate, lb-mol/min-ft^2

V_t = liquid volume, gal

C_{O_2} = concentration of oxygen in the air in terms of Vt, lb-mol/gal

R = gas constant, atm-gal/lb-mol-^{o}R

T = gas temperature, ^{o}R

h_t = liquid depth, ft

P_T = total pressure, atm

K_La = overall oxygen transfer coefficient, 1/min

H = Henry's Law constant, atm-gal/lb-mol

It is assumed that oxygen absorption is the limiting factor, that the liquid phase is perfectly mixed, that the gas is in plug flow, that the liquid oxygen concentration is zero (the oxidation reaction is instantaneous), and that the oxygen behaves as an ideal gas.

K_La is based on experimental data and is expressed as:

$$K_La^{Pred} = [21112544][h_t^{-0.985}][I^{0.474}][G_a^{0.315}][pH^{-2.098}] \qquad \text{-14-}$$
$$[D_t^{-2.876}][N^{0.806}][D_s^{2.37}]$$

where

I = ionic strength

D_h = tank diameter, ft

N = mixer rpm

D_s = sparger hole diameter, in.

The role of the hold tank geometry and the mixer are evident. The application of this model to the Shawnee test facility and Widows Creek test results is discussed in the results section.

Power Consumption

These equations can also be used to determine total power consumption since both the air rate and the mixer rpm appear in them. The power requirements for the mixer can be expressed (88) in horsepower.

$$hp = (0.4)(N^3)(D^5)(spGr/(320)^5) \qquad -15-$$

where

D = turbine diameter, in.

N = mixer speed, rpm

SpGr = specific gravity

Power to compress the air can be obtained from standard texts (89). Figure 13 shows the relationship of total power - air compression plus mixer - for the Widows Creek venturi hold tank for 95% oxidation at 1.007 lb mol/min using a specific gravity of 1.07, a mixer speed that allows the air rate to vary as defined by equations -13- and -14-. The horsepower is obtained from equation -15-. It appears that the Widows Creek venturi system operates near the point of minimum power based on these equations.

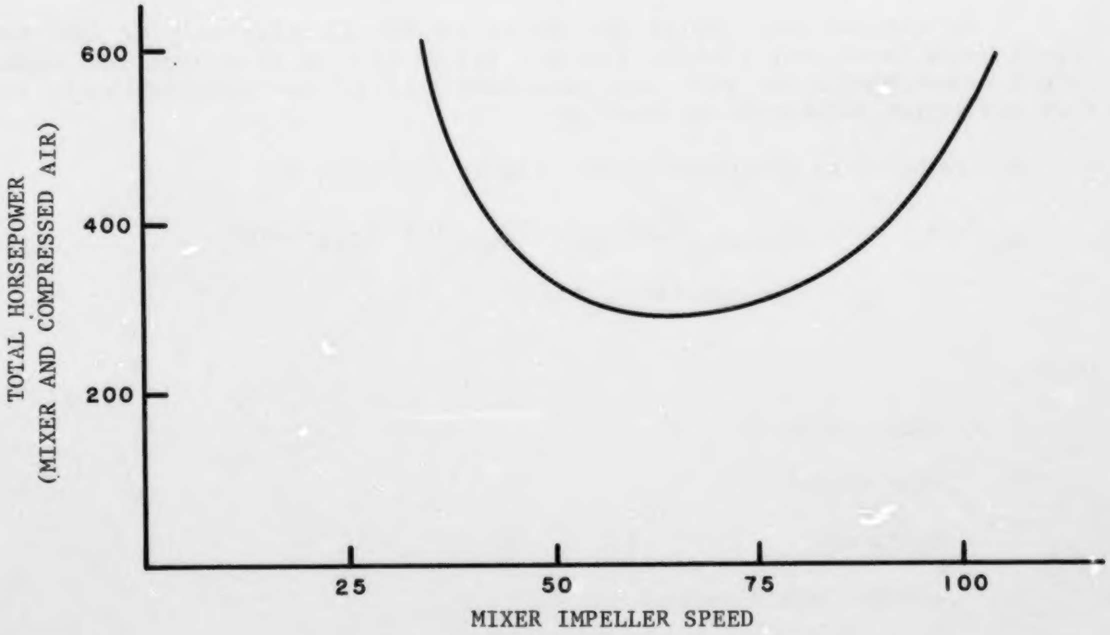


Figure 13. Total power versus impeller speed.

Gypsum precipitation can be represented by the equation (11):

$$r = kafc\ (RS-1) \qquad -16-$$

where

r = precipitation rate, g/L-s

k = temperature dependent constant, g/cm^2-s-unit driving force

a = crystal area, cm^2/g

f = weight fraction of the precipitation species in the solid phase

c = total solids, g/L

RS = relative saturation $CaSO_4 \cdot 2H_2O$

In a system with fixed conditions of temperature and total solids such as Widows Creek the precipitation rate is a function of the crystal area and the relative saturation. It is evident that to avoid high supersaturation levels that could cause scaling a sufficient crystal area must be maintained. It is also evident from results that indicate a low level of supersaturation in forced-oxidation processes (9) that the crystal area is sufficient. A factor of possible importance is agitation which tends to shatter the crystals, thus increasing crystal area, as well as initiate homogeneous nucleation (31).

TEST PLAN AND OPERATING CONDITIONS

OBJECTIVES

The general objectives of the Widows Creek forced-oxidation tests were to demonstrate forced oxidation as a practical method of producing a waste suitable for landfill disposal and to acquire the data needed to design full-scale systems on units 7 and 8. In terms of specific objectives the goals were to attain a minimum of 95% oxidation and a waste that could be dewatered to at least 80% solids over a range of conditions sufficient to define the optimum design and operating conditions. The objectives had, of course, to be attained within the requirements of the 88% SO_2 removal to be required for units 7 and 8.

TEST PLAN

The test plan evolved to meet these objectives (7), based on available data within TVA, operating experience at the Shawnee test facility, and published work, consisted of three series of tests:

A series: Oxidation in the absorber (spray tower) hold tank
B series: Oxidation in the venturi hold tank
C series: Oxidation in both the absorber and venturi hold tanks

These three oxidation modes would demonstrate venturi hold tank and absorber hold tank forced oxidation as well as a combination of both, allowing a determination of the method best suited to the Widows Creek system. A primary criterion, in addition to attaining the oxidation and dewatering goals, was the minimum air stoichiometry attainable under each of the three oxidation modes.

As an aid in defining the initial operating conditions, forced-oxidation tests were made at the Shawnee test facility venturi - spray tower system using Widows Creek Unit 8 coal and limestone (69). For the C-series test condition simulations, with oxidation in both the spray tower and venturi hold tank, a portion of the venturi recirculation slurry returned to the spray tower to simulate the carryover believed to occur at Widows Creek. The major test conditions and results are shown in Table 5. Based in part on these results, the initial operating conditions of the Widows Creek demonstration tests were established as shown in Table 6. From these initial conditions, some conditions would be systematically varied to provide a range of operating conditions.

TABLE 5. WIDOWS CREEK UNIT 8 SIMULATION TESTS AT THE SHAWNEE TEST FACILITY

Major Test Conditions[a]	827-1A	828-1A	828-1B	829-1A	830-1A
Fly ash loading, approximate gr/dsft^3	5	5	5	5	5
Gas rate, aft^3/min at 300°F	35,000	35,000	35,000	35,000	35,000
Venturi liquid rate, gal/min	600	600	600	600	600
Spray tower liquid rate, gal/min	1,500	1,500	1,500	1,500	1,500
Venturi, % solids (controlled)	12	12	12	12	12
Residence times, (min)/tank level (ft):					
Spray tower hold tank	9.4/6	9.4/6	9.4/6	9.4/6	9.4/6
Venturi hold tank	11.3/18	11.3/18	11.3/18	11.3/18	11.3/18
Venturi inlet pH (controlled)	5.5	5.5	b	5.5	6.0
Sparger air rate, sft^3/min	250	180	180	145	250
Back mix[c], gal/min	65	65	65	65	29
Selected Results					
Start of run date	2/14/79	3/12/79	3/13/79	3/16/79	3/22/79
Onstream hours	345	29	48	106	150+
SO_2 removal, %	74	82	59	81	88
Inlet SO_2 concentration, ppm	2,800	2,550	2,750	2,850	2,700
Spray tower, % solids	10.7	10.8	10.2	10.5	10.2
Venturi inlet pH	5.5	5.6	5.3	5.6	6.1
Spray tower inlet pH	5.6	5.7	5.0	5.7	6.0
Spray tower limestone stoichiometric ratio	1.95	2.7	2.1	1.7	2.3
Spray tower inlet liquid gypsum saturation, %	101	95	109	91	92
Spray tower sulfite oxidation, %	73	71	89	66	56
Overall sulfite oxidation, %	98.1	97.7	98.4	87.5	95.2
Overall limestone utilization, %	62	47	69	70	57
Venturi inlet liquid gypsum saturation, %	97	96	91	93	98
Venturi inlet liquid SO_3 concentration, ppm	63	101	63	166	235
Air stoichiometry, atoms O/lb mole SO_2 absorbed	2.12	1.51	1.95	1.10	1.85
Filter cake solids, wt %	85	83	82	79	81

Source: (90)

a. All runs used Widows Creek coal and limestone.

b. Venturi stoichiometry controlled at 1.3.

c. Back mix simulates limestone slurry carryover between the venturi and absorber tanks.

TABLE 6. PRINCIPAL PROPOSED OPERATING CONDITIONS

	Series		
	A	B	C
Flue gas rate, aft^3/min	400,000	400,000	400,000
Flue gas SO_2 ppm, volume	3,000-3,500	3,000-3,500	3,000-3,500
Additive stoichiometry	Normal	Normal	1.1
Venturi ΔP, in. H_2O	5	5	5
Slurry feed rate, gal/min			
Venturi	3,400	3,400	3,400
Absorber	20,000	20,000	20,000
Effluent hold tank level, ft			
Venturi	21	21	21
Absorber	23	23	23
Slurry solids content, %			
Venturi	15	15	15
Absorber	15	15	15
Tank mixer power, hp			
Venturi	75	75	75
Absorber	140	300	300
Forced air stoichiometry[a]	2.0	2.0	X[b]

Source: (9)

a. lb atoms O/lb mol SO_2 absorbed, to be varied to minimize at 95% oxidation.

b. The minimum air rate required, as determined in the A and B series.

Since the dewatering system objectives could be determined without treatment of the full effluent stream, a dewatering system to treat 10% of the effluent was specified. The primary variables to be studied were thickener underflow recycle rate and filter vacuum and drum speed. The dewatering system design feed rate was 46 gal/min of oxidized slurry containing 16% solids.

The test plan specified data recording and sampling procedures. A sampling schedule is shown in Table 7. Sampling and analytical procedures are shown in Appendix B.

ACTUAL OPERATING CONDITIONS

A number of conditions and events precluded a strict adherence to the test plan. Before the forced-oxidation tests began, the A series (oxidation in the absorber hold tank) was rescheduled to take place last. This was done because the B series, oxidation in the venturi hold tank, appeared to offer the best probability of an efficient oxidation process at the lowest air stoichiometry because of the lower pH in the venturi hold tank.

The actual test schedule also differed in several respects from the test plan. In most cases this was due to the cyclic and intermittent operation of the boiler during the test period or to the need to modify or repair the

TABLE 7. SAMPLING PLAN

Sample point	Frequency	Sampling group	Analysis	Where analyzed
51	Every 2 h	TVA TVF operator	Slurry - ph, % solids T (°F)	WC
51	SSTP	Radian	Slurry - pH, % solids T (°F), filter leaf test, settling rate test	WC
51	SSTP	Radian	Solids - SO_3, SO_4, Ca, Mg, acid insolubles	WC
51	SSTP	Radian	Liquid - SO_3, SO_4, Ca, Mg, Cl	WC
51	SSTP	Radian	Solid - CO_3 Liquid - CO_3	TVA - PSC Radian
51	Bimonthly	Radian	Liquids - NO_3, NH_3	TVA - PSC
51	Bimonthly	Radian	Liquid - Na, K	WC
510	Every 2 h	TVA shift chemist	Slurry - pH, % solids T (°F)	WC
511	Every 2 h	TVA shift chemist	Slurry - pH, % solids T (°F)	WC
52	Every 2 h	TVA TVF operator	Slurry - pH, % solids	WC
52	SSTP	Radian	Slurry - pH, % solids T (°F), filter leaf test, settling rate test	WC
52	SSTP	Radian	Solids - SO_3, SO_4, Ca, Mg, acid insolubles, particle size distribution	WC
53	Every 2 h	TVA TVF operator	Slurry - pH, % solids	WC
53	SSTP	Radian	% solids, SO_3, SO_4	WC
52	SSTP	Radian	Particle size distribution	MS, RB
-	Biweekly	EN RES	SO_2 - Flow traverse (inlet and outlet)	WC

WC - Widows Creek
SSTP - Steady-state test point
TVF - Thickener and vacuum filter
PSC - Power Service Center
MS, RB - Muscle Shoals Research Branch

oxidation and dewatering equipment. The generalized operating schedule of the D-train system and forced-oxidation testing is shown in Figure 14. The effect of the relatively frequent shutdowns was to extend the testing period.

Other operational- and equipment-related problems with a bearing on the forced-oxidation testing were:

- Oxidation air rates were initially limited by an undersized air flow indicator. When this was replaced air rates were limited by the size of the venturi tank and agitator and difficulties in maintaining the absorber hold tank liquid level.
- Entrainment of venturi liquid created a considerable backflow, limiting the degree to which pH, solids, and tank levels could be controlled in the venturi liquid system.
- Gas flow measurements, as determined by the ID fan power, were difficult and were complicated by load variations and changes in upstream equipment such as air heater fouling.
- The dewatering system was oversized for the 10% sidestream and did not provide rate data suitable for scale-up use to the extent that the filter-leaf tests did.

These conditions, and a variety of short-term situations, influenced to some extent the course and progress of the test program, as well as the interpretation of the results. Factors influencing the interpretation of the data are discussed where pertinent. The primary effects of these conditions, however, were to extend the test period, to prevent a comprehensive spectrum of B-series and all C-series tests, and to preclude qualitative scale-up data on dewatering. The general objectives were not materially affected.

The actual FGD test conditions differed from the test plan conditions in some respects. Of particular significance are the flue gas rates, flue gas SO_2 content, limestone stoichiometry, and air stoichiometry. The actual flue gas rates were lower and generally fluctuated throughout the test period because of the load following nature of the power unit operation. The SO_2 content of the flue gas was low because coal with lower than normal sulfur was being used. Limestone stoichiometry varied with normal operating procedures to control the venturi hold tank pH at a fixed level. The air stoichiometries of tests identified as B-1 and B-2 were low because of limitations in the air system. Beginning with tests identified as B-2A, the air stoichiometries were limited by the stress (rev/min) that could be placed on the venturi hold tank agitator and the volume of air that could be injected into the venturi hold tank.

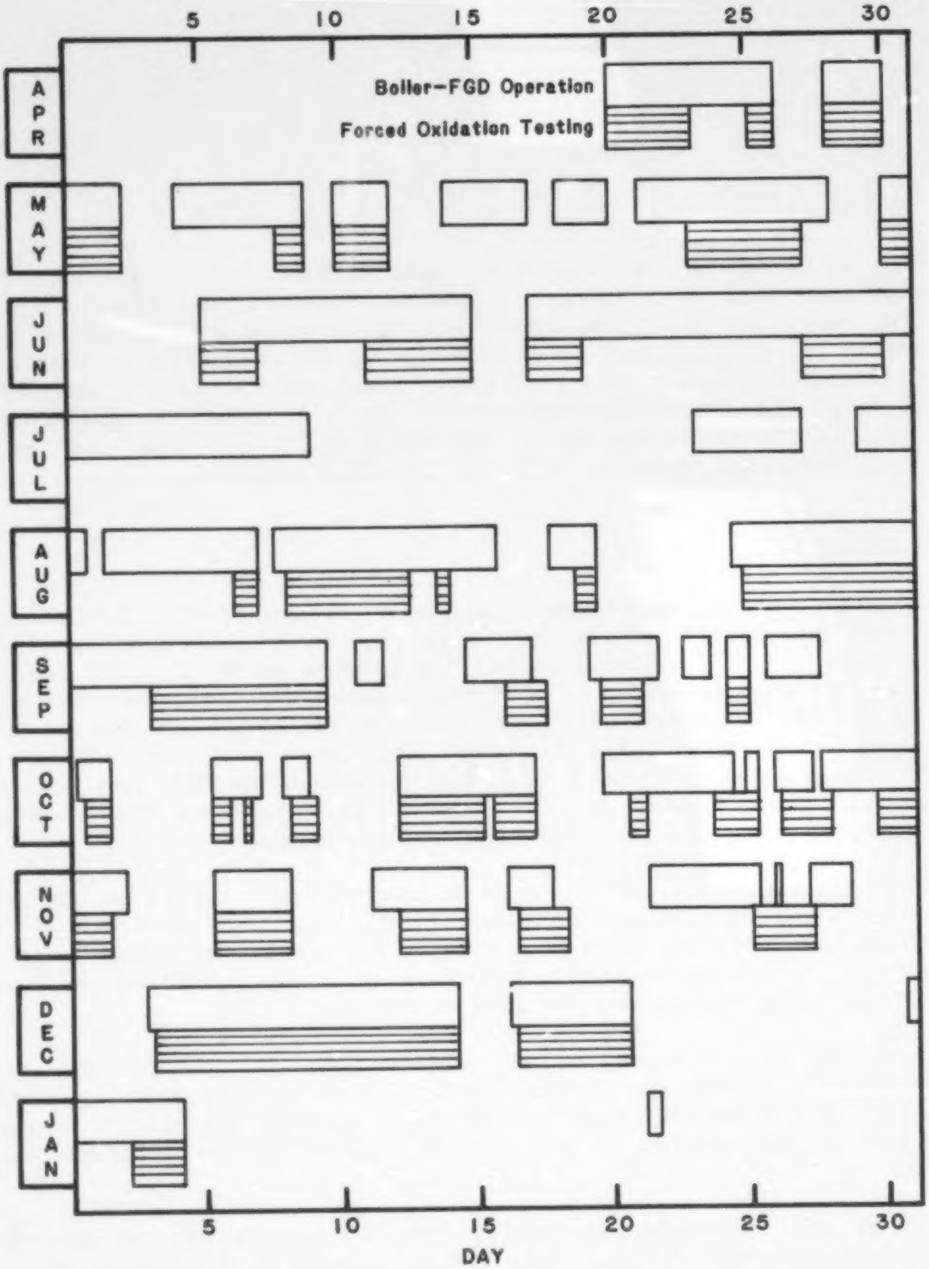


Figure 14. FGD system availability and forced-oxidation test periods.

RESULTS

The two phases of study in the Widows Creek forced-oxidation demonstration test were forced oxidation itself and dewatering of the resulting waste sludge. The forced-oxidation phase was primarily concerned with definition of oxidation level in terms of the oxidation configuration and air stoichiometry while the dewatering phase was primarily concerned with definition of the dewatering characteristics in terms of the oxidation level. Combined, the two phases served to meet the overall test objective, production of a highly oxidized waste suitable for landfill disposal.

FORCED OXIDATION

A summary of operating conditions and average results for steady-state run conditions is shown in Table 8. Average analytical data on bleedstream (sample point 51) and thickener underflow (sample point 52) are shown for the same runs in Table 9. Average analytical data on absorber bottoms are shown in Table 10. All B-series tests were run with oxidation air sparged only into the venturi hold tank. All C-series tests were run with 20% of the air sparged into the venturi hold tank and the remaining 80% into the absorber hold tank. The D-series is the same as the C-series; the D designation denotes use of the waste in a landfill demonstration.

The operating condition data show the variable nature of the flue gas flow. The flue gas SO_2 content ranged from about 1,300 to 2,400 ppm and was usually in the 1,700 to 2,000 ppm range. SO_2 removal efficiency was usually in the high 70% to low 80% range during the B-series tests and increased into the high 80% range during the C-series tests.

Limestone stoichiometry varied widely from 1.1 to 2.0 mol $CaCO_3$/mol SO_2 absorbed. Limestone stoichiometry had no discernable effect on oxidation. Solids in the recirculated liquid also varied widely, ranging from 4% to 30% in the venturi loop. Again, solids had no apparent effect on oxidation.

The pH of the bleedstream ranged from 5.0 to 5.9 (in one case 6.3) but was generally between 5.4 and 5.8. This pH probably represents the approximate oxidation conditions.

The bleedstream magnesium content was generally in the range of 200 to 500 mg/L and the chloride level was generally in the range of 500 to 1,800 mg/L. These are roughly compensating concentrations in terms of their effect on SO_2 removal according to published data (16). Probably neither magnesium nor chloride influenced the results through chemical effects, as discussed in the background section.

TABLE 8. OPERATING CONDITIONS AND RESULTS SUMMARY

Conditions	Run:	B-1	B-1	B-1	B-2	B-2	B-2A	B-2A	B-2A	B-2A
	Date:	4/20	4/22	4/23	4/30	5/1	5/8	5/10	5/11	5/14
Flue gas										
kft^3/min (1 atm, 60°F)		250	210	220	260	270	300	245	320	320
SO_2 in, ppm (vol)		1,340	1,840	1,670	1,700	1,620	2,010	1,650	1,850	1,900
SO_2 out, ppm (vol)		210	350	290	440	400	430	130	390	490
SO_2 removal, %		84	81	83	74	75	79	92	79	74
Limestone stoichiometry		1.4	1.2	1.6	1.3	1.2	1.2	1.2	1.1	1.3
Venturi										
Recirculation, gpm		3,400	3,400	3,400	3,400	3,400	3,400	3,400	3,400	3,400
Solids, %		13	8	8	9	14	14	7	12	12
pH										
Absorber										
Recirculation, gpm		20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000
Solids, %		12	8	8	9	12	13	5	10	10
Air stoichiometry[a]		0.8	0.4	0.7	0.7	0.8	1.5	2.8	1.5	2.1
Bleedstream										
°F		114	114	114	111	-	104	108	117	117
pH		5.7	5.5	5.5	5.9	5.8	5.6	5.6	5.4	5.5
Oxidation, %		40	32	36	62	63	67	99	81	72
Filter cake										
Solids, %		61	70	65	68	68	71	74	79	75

(continued)

TABLE 8 (continued)

Conditions	Run:	B-2A	B-2A	B-2	B-2	B-2	B-2B	B-2	C-1	C-1
	Date:	5/15	5/16	5/24	5/25	5/26	5/31	6/1	6/27	6/29
Flue gas										
kft^3/min (1 atm, 60°F)		300	305	300	280	260	270	270	390	380
SO_2 in, ppm (vol)		1,840	1,870	1,810	1,540	1,890	1,930	2,380	1,900	1,700
SO_2 out, ppm (vol)		350	400	610	360	350	400	520	320	250
SO_2 removal, %		81	79	66	77	81	79	78	83	85
Limestone stoichiometry		1.3	1.2	1.2	1.2	1.1	1.2	1.1	1.4	1.5
Venturi										
Recirculation, gpm		3,400	3,400	3,400	3,400	3,400	3,400	3,400	3,400	3,400
Solids, %		14	15	10	11	11	10	13	9	9
pH									6.4	6.0
Absorber										
Recirculation, gpm		20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000
Solids, %		14	13	10	10	10	8	10	10	10
Air stoichiometry[a]		1.7	1.4	1.7	1.7	2.1	2.4	2.0	2.8	2.7
Bleedstream										
°F		109	111	122	115	117	118	118	124	122
pH		5.4	5.8	5.8	5.6	5.7	5.5	5.3	5.8	5.7
Oxidation, %		86	77	75	79	79	91	99	99	99
Filter cake										
Solids, %		77	80	-	70	69	-	-	82	83

(continued)

TABLE 8 (continued)

Conditions	Run: Date:	C-2A 8/11	C-2B 8/20	C-2C 8/27	C-3D 8/28	C-3D 8/29	C-3D 8/30	C-3D 8/31	C-3D 9/1	C-2E 9/5
Flue gas										
kft^3/min (1 atm, 60°F)		307	334	306	304	332	325	323	310	340
SO_2 in, ppm (vol)		1,913	-	-	2,017	2,459	2,108	2,017	1,900	1,967
SO_2 out, ppm (vol)		279	-	-	376	373	317	318	316	404
SO_2 removal, %		85	-	-	81	85	85	84	83	79
Limestone stoichiometry		1.3	2.0	1.2	1.3	1.3	1.3	1.3	1.7	1.6
Venturi										
Recirculation, gpm										
Solids, %		11	16	15	16	13	12	12	15	19
pH										
Absorber										
Recirculation, gpm										
Solids, %										
pH										4.8
Oxidation, %										84
Air stoichiometry[a]		2.1	2.1	2.2	2.2	1.8	1.8	1.7	1.9	2.1
Bleedstream										
°F		122	118	118	124	120	118	118	120	122
pH		5.5	5.5	5.2	5.2	5.2	5.1	5.3	5.1	5.0
Oxidation, %		99	98	99	99	97	95	98	94	82
Filter cake										
Solids, %		79	-	-	-	-	-	-	-	-

(continued)

TABLE 8 (continued)

Run:	C-2E	C-2E	C-2E	C-2F	C-2F	C-2G	C-2H	C-2T	C-2T
Conditions Date:	9/6	9/7	9/8	9/20	9/21	9/25	10/2	10/31	11/1
Flue gas									
kft^3/min (1 atm, 60°F)	344	324	300	328	361	326	274	308	303
SO_2 in, ppm (vol)	1,967	1,783	1,909	-	1,971	1,988	-	1,607	1,760
SO_2 out, ppm (vol)	308	318	258	-	381	380	-	-	197
SO_2 removal, %	84	82	86	-	81	81	-	-	89
Limestone stoichiometry	1.5	1.6	1.4	1.2	1.9	1.1	1.1	1.1	2.0
Venturi									
Recirculation, gpm									
Solids, %	15	11	13	7	13	9	11	4	19
pH									
Absorber									
Recirculation, gpm									
Solids, %									
pH							4.5	-	5.2
Oxidation, %							91	99	99
Air stoichiometry[a]	1.9	2.0	1.6	1.9	1.8	1.7	1.9	1.6	1.7
Bleedstream									
°F	120	122	117	111	118	115	108	108	118
pH	5.3	5.4	5.4	5.4	5.3	5.4	5.1	5.4	5.4
Oxidation, %	91	94	93	99	91	94	96	99	100
Filter cake									
Solids, %	-	-	77	-	86	76	-	-	-

(continued)

TABLE 8 (continued)

Conditions Run:	C-2T	D-1	D-1	D-2	D-2	D-4	D-4	D-4	D-4
Date:	11/2	11/14	11/15	11/18	11/19	12/6	12/8	12/9	12/10
Flue gas									
kft^3/min (1 atm, 60°F)	303	287	303	293	298	339	333	326	328
SO_2 in, ppm (vol)	1,679	-	-	-	-	1,442	1,725	1,852	1,750
SO_2 out, ppm (vol)	185	-	-	-	-	144	257	268	280
SO_2 removal, %	89	-	-	-	-	90	85	86	84
Limestone stoichiometry	2.2	1.4	2.1	1.4	1.9	-	1.2	1.1	1.3
Venturi									
Recirculation, gpm									
Solids, %	30	4	19	4	14	-	13	7	9
pH									
Absorber									
Recirculation, gpm									
Solids, %									
pH	5.2	4.9	5.1		5.4	5.6	5.0		5.5
Oxidation, %	100	99	99		99	98	97		95
Air stoichiometry[a]	1.8	1.8	2.0	1.7	1.6	1.9	1.8	1.7	1.7
Bleedstream									
°F	117	108	108	106	111	109	102	109	109
pH	5.1	5.0	5.1	5.3	6.3	5.9	5.8	5.5	5.6
Oxidation, %	100	99	99	98	99	-	99	97	95
Filter cake									
Solids, %	-	-	87	85	86	-	90	-	-

(continued)

TABLE 8 (continued)

Conditions	Run:	D-4	D-4	D-4	D-4	D-5	D-5	D-5	D-6
	Date:	12/11	12/12	12/13	12/14	12/19	12/20	12/21	1/4/81
Flue gas									
kft^3/min (1 atm, 60°F)		322	323	353	355	339	337	296	300
SO_2 in, ppm (vol)		1,717	1,742	1,742	1,892	1,844	1,579	1,325	1,800
SO_2 out, ppm (vol)		222	202	245	248	214	164	160	181
SO_2 removal, %		87	88	86	87	87	90	88	90
Limestone stoichiometry		1.3	1.5	1.1	1.9	1.6	1.4	1.0	1.3
Venturi									
Recirculation, gpm									
Solids, %		10	10	7	22	17	8	3	17
pH									
Absorber									
Recirculation, gpm									
Solids, %									
pH		5.4	5.4	5.2	5.4	5.5	5.5	5.4	5.5
Oxidation, %		98	100	99	99	97	83	97	99
Air stoichiometry[a]		1.9	1.7	1.5	1.7	2.1	2.3	2.8	-
Bleedstream									
°F		106	113	106	108	106	106	97	106
pH		5.8	5.5	5.4	5.3	5.8	5.7	5.4	5.6
Oxidation, %		98	99	98	98	97	99	100	99
Filter cake									
Solids, %		89	-	-	-	87	87	-	90

[a] lb atoms O/lb moles SO_2 absorbed.

TABLE 9. BLEEDSTREAM AND THICKENER UNDERFLOW ANALYTICAL DATA

Sample point	Sample Run: Date:	No oxidation 5/21	B-1 4/20	B-1 4/22	B-1 4/23	B-2 4/30	B-2 5/1	B-2A 5/8	B-2A 5/10	B-2A 5/11
51	**Bleedstream**									
	°F	122	115	115	115	111	-	104	108	117
	pH	5.1	5.7	5.5	5.5	5.9	5.8	5.6	5.6	5.4
	Liquid, mg/L									
	Ca		930	1,230	1,140	1,300	1,030	1,080	946	1,140
	SO_3	507	140	360	330	140	80	130	70	150
	SO_4	1,790	2,100	2,090	1,800	1,200	1,670	1,790	1,890	1,890
	CO_3	132	120	120	120	140	140	90	66	84
	Mg	525	501	309	389	281	270	445	349	477
	Cl	2,353	1,420	760	1,150	1,440	1,310	1,700	1,120	1,380
	Rel. sat., SO_3	2.7	1.4	2.8	2.7	2.5	1.1	1.2	0.6	1.1
	Rel. sat., SO_4	1.0	1.2	1.3	1.1	1.3	1.0	1.0	1.1	1.1
	Solids, mg/g									
	Ca		176	198	184	185	177	174	158	146
	SO_3		158	224	172	110	109	98	4	51
	SO_4		112	126	114	211	222	240	317	257
	CO_3		-	-	-	52	42	42	51	45
	Mg		6	4	6	4	4	3	3	3
	Acid insoluble		385	293	290	310	344	342	353	374
	Oxidation, %	39	40	32	36	62	63	67	99	81
52	**Thickener Underflow**									
	pH		6.1	6.2	5.9	6.3	6.3	5.9	5.6	5.9
	Solids, mg/g									
	Ca		192	221	213	196	185	180	165	176
	SO_3		125	138	108	89	66	70	0	54
	SO_4		138	53	80	182	228	256	290	234
	CO_3		-	-	-	123	93	65	86	87
	Mg		6	7	8	5	5	4	4	4
	Acid insoluble		365	255	285	297	320	321	325	355
	Oxidation, %		48	24	38	63	74	75	99	78

(continued)

TABLE 9 (continued)

Sample point	Sample Run: / Date:	B-2A 5/14	B-2A 5/15	B-2A 5/16	B-2 5/24	B-2 5/25	B-2 5/26	B-2B 5/31	B-2 6/1	C-1 6/27
51	**Bleedstream**									
	°F	117	109	111	122	115	117	118	118	124
	pH	5.5	5.4	5.8	5.7	5.6	5.7	5.5	5.3	5.8
	Liquid, mg/L									
	Ca	1,150	1,090	1,140	978	1,040	990	1,090	1,070	1,010
	SO_3	270	190	170	220	88	170	140	56	8
	SO4	1,560	1,600	2,020	1,590	1,760	1,770	1,560	1,650	1,600
	CO_3	130	90	78	90	72	84	60	42	-
	Mg	513	541	513	325	433	369	457	469	330
	Cl	1,380	1,580	1,500	856	1,180	1,120	1,340	1,430	1,120
	Rel. sat., SO_3	2.2	1.3	2.2	2.4	0.8	1.8	1.2	0.3	0.1
	Rel. sat., SO4	0.9	0.9	1.1	0.9	1.0	1.0	0.9	1.0	1.0
	Solids, mg/g									
	Ca	178	188	174	183	196	207	181	166	1
	SO_3	75	41	64	79	67	78	28	1	0
	SO4	231	287	259	279	310	347	348	354	301
	CO_3	53	98	65	51	48	50	-	-	-
	Mg	3	3	3	3	3	3	2	1	2
	Acid insoluble	344	284	339	272	247	272	270	315	394
	Oxidation, %	72	86	77	75	79	79	91	99+	99+
52	**Thickener Underflow**									
	pH	5.6	6.0	6.0	5.9	6.1	6.4	6.5	6.0	6.4
	Solids, mg/g									
	Ca	199	179	174	192	201	217	194	171	180
	SO_3	63	60	58	70	56	56	32	1	0
	SO4	194	294	231	280	308	350	341	373	296
	CO_3	117	27	73	51	70	91	-	-	306
	Mg	4	3	3	3	3	3	2	1	2
	Acid insoluble	313	321	350	254	228	263	245	283	366
	Oxidation, %	72	81	77	77	82	84	90	99+	100

(continued)

TABLE 9 (continued)

Sample point	Sample	Run: Date:	C-1 6/29	C-2A 8/11	C-2B 8/20	C-2C 8/27	C-2D 8/28	C-2D 8/29	C-2D 8/30	C-2D 8/31	C-2D 9/1
51	**Bleedstream**										
	°F		122	123	120	118	124	120	118	118	120
	pH		5.7	5.6	5.4	5.2	5.2	5.2	5.1	5.3	5.1
	Liquid, mg/L										
	Ca		974	1,162	1,253	1,062	1,295	1,255	1,182	1,114	1,050
	SO_3		2	890	850	153	889	1,257	598	713	801
	SO_4		1,670	1,357	1,585	1,643	1,316	1,527	1,566	1,575	1,374
	CO_3		-	168	145	151	-	114	124	147	-
	Mg		260	240	266	280	333	227	227	198	189
	Cl		969	1,174	1,450	1,595	1,858	1,411	1,255	1,092	982
	Rel. sat., SO_3		1.2	3.2	4.7	0.7	4.1	5.6	2.5	3.9	2.8
	Rel. sat., SO_4		1.0	0.9	0.9	0.9	0.8	0.9	1.0	0.9	0.8
	Solids, mg/g										
	Ca		197	171	226	167	181	176	190	182	220
	SO_3		1	4	8	2	2	7	14	6	17
	SO_4		310	333	282	332	323	315	330	332	305
	CO_3		-	69	188	59	65	82	67	115	108
	Mg		2	2	4	2	2	2	1	2	2
	Acid insoluble		339	292	191	275	257	246	225	247	242
	Oxidation, %		99+	99	97	99	99	97	95	98	94
52	**Thickener Underflow**										
	pH		6.1								
	Solids, mg/g										
	Ca		189	169	222	173	191				
	SO_3		0	26	7	42	7				
	SO_4		299	280	293	265	264				
	CO_3		119	69	182	76	98				
	Mg		2	2	3	2	2				
	Acid insoluble		345	322	198	309	259				
	Oxidation, %		99+								

(continued)

TABLE 9 (continued)

Sample point	Sample	Run: Date:	C-2E 9/5	C-2E 9/6	C-2E 9/7	C-2E 9/8	C-2F 9/20	C-2F 9/21	C-2G 9/25	C-2H 10/2	C-2T 10/31
51	**Bleedstream**										
	°F		122	120	122	117	111	118	115	108	108
	pH		5.0	5.3	5.4	5.4	5.4	5.3	5.4	5.1	5.4
	Liquid, mg/L										
	Ca		1,439	1,050	1,070	1,090	782	1,058	1,048	710	1,002
	SO_3		1,361	833	817	719	12	370	404	-	416
	SO_4		1,623	1,623	1,585	1,566	1,700	1,643	2,243	2,080	1,518
	CO_3		-	164	168	141	176	176	151	148	129
	Mg		333	306	187	215	197	253	226	253	209
	Cl		1,790	1,149	822	1,000	791	1,305	815	511	1,141
	Rel. sat., SO_3		4.7	3.7	5.7	4.7	0.1	1.9	3.7	0.0	2.7
	Rel. sat., SO_4		0.9	0.9	0.9	0.9	0.9	0.9	1.3	0.9	0.9
	Solids, mg/g										
	Ca		204	194	217	185	216	214	184	163	153
	SO_3		46	22	16	19	5	22	18	12	2
	SO_4		256	286	304	284	418	235	326	345	342
	CO_3		121	112	132	87	61	17[illegible]	64	36	-
	Mg		4	4	3	2	3	[illegible]	3	1	2
	Acid insoluble		263	258	209	261	300	246	364	294	340
	Oxidation, %		82	91	94	93	99	91	93	95	99
52	**Thickener Underflow**										
	pH										
	Solids, mg/g										
	Ca		200				179		218	165	
	SO_3		57				12		34	12	
	SO_4		280				293		334	354	
	CO_3		93				116		89	36	
	Mg		3				3		4	1	
	Acid insoluble		257				255		378	302	
	Oxidation, %										

(continued)

TABLE 9 (continued)

Sample point	Sample	Run:	C-2T	C-2T	D-1	D-1	D-2	D-2	D-4	D-4	D-4
		Date:	11/1	11/2	11/14	11/15	11/18	11/19	12/6	12/8	12/9
51	Bleedstream										
	°F		118	117	108	108	106	111	109	102	109
	pH		5.4	5.1	5.0	5.1	5.3	6.3	5.9	5.8	5.5
	Liquid, mg/L										
	Ca		1,130	1,090	1,070	1,090	966	1,050	914	749	822
	SO_3		616	793	788	897	704	584	7	2	3
	SO_4		1,671	1,729	1,595	1,652	1,864	1,614	1,556	1,700	1,681
	CO_3		118	133	125	114	138	180	114	102	174
	Mg		321	246	220	219	135	183	137	145	146
	Cl		1,659	1,106	971	954	376	993	879	560	741
	Rel. sat., SO_3		3.9	3.0	2.3	3.5	3.6	1.4	0.1	0.0	0.0
	Rel. sat., SO_4		0.9	1.0	0.9	1.0	1.1	0.9	1.0	0.9	1.0
	Solids, mg/g										
	Ca		220	231	168	235	182	215	-	165	147
	SO_3		1	1	2	2	4	2	-	3	9
	SO_4		262	252	285	264	298	272	-	332	303
	CO_3		-	-	-	-	-	182	-	59	26
	Mg		5	5	5	4	3	3	-	2	2
	Acid insoluble		210	199	336	189	304	215	-	334	413
	Oxidation, %		99+	99+	99	99	98	99	-	99	97
52	Thickener Underflow										
	pH										
	Solids, mg/g										
	Ca				217		219			189	
	SO_3				2		2			5	
	SO_4				292		271			310	
	CO_3				-		191			101	
	Mg				3		4			3	
	Acid insoluble				218		223			250	
	Oxidation, %										

(continued)

TABLE 9 (continued)

Sample point	Sample	Run:	D-4	D-4	D-4	D-4	D-4	D-5	D-5	D-6
		Date:	12/10	12/11	12/12	12/13	12/14	12/19	12/20	1/4/80
51	Bleedstream									
	°F		109	106	113	106	108	106	106	106
	pH		5.6	5.8	5.5	5.4	5.3	5.8	5.7	5.6
	Liquid, mg/L									
	Ca		1,002	705	902	705	914	994	770	886
	SO_3		14	30	366	49	463	150	19	793
	SO_4		1,719	1,748	1,758	1,748	1,758	1,960	1,278	1,739
	CO_3		162	192	186	148	173	234	144	186
	Mg		190	117	105	179	161	209	163	217
	Cl		709	379	425	507	610	1,014	1,021	705
	Rel. sat., SO_3		1.4	0.3	2.7	0.3	2.3	1.9	0.2	6.4
	Rel. sat., SO_4		1.1	1.0	1.1	0.9	1.0	1.1	0.7	0.9
	Solids, mg/g									
	Ca		177	190	194	141	215	202	177	191
	SO_3		13	7	2	6	6	9	3	2
	SO_4		321	336	313	305	271	296	303	345
	CO_3		75	90	134	-	160	166	91	100
	Mg		2	2	3	2	3	3	3	2
	Acid insoluble		208	240	239	377	187	176	279	-
	Oxidation, %		95	98	99	98	98	97	99	99
52	Thickener Underflow									
	pH									
	Solids, mg/g									
	Ca							194		
	SO_3							7		
	SO_4							317		
	CO_3							109		
	Mg							2		
	Acid insoluble							219		
	Oxidation, %									

TABLE 10. ABSORBER BOTTOMS ANALYTICAL DATA

Sample	Run:	C-2E	C-2H	C-2T	C-2T	C-2T	D-1	D-1	D-2	D-4
	Date:	9/5	10/2	10/31	11/1	11/2	11/14	11/15	11/19	12/6
Absorber Bottoms										
°F		127	117	108	113	106	108	109	109	115
pH		4.8	4.5	-	5.2	5.2	4.9	5.1	5.4	5.6
Liquid, mg/L										
Ca		1,359	792	1,018	1,070	1,038	1,030	1,078	1,058	962
SO_3		849	480	283	296	347	330	616	384	384
SO_4		2,152	2,065	1,758	1,969	1,979	2,017	1,912	1,873	1,739
CO_3		-	196	112	139	151	164	144	252	102
Mg		328	238	253	297	231	220	220	205	112
Cl		1,510	401	1,202	1,273	840	883	798	900	613
Rel. sat., SO_3		1.8	0.3	1.2	1.3	1.5	0.8	2.4	2.5	3.6
Rel. sat., SO_4		1.2	1.0	1.0	1.1	1.1	1.2	1.1	1.1	1.1
Oxidation, %		84	91	99	99	99+	99	99	99	98

(continued)

TABLE 10 (continued)

Sample	Run:	D-4	D-4	D-4	D-4	D-4	D-4	D-5	D-5	D-6
	Date:	12/8	12/10	12/11	12/12	12/13	12/14	12/19	12/20	1/4/80
Absorber Bottoms										
°F		109	106	108	113	118	108	109	97	106
pH		5.0	5.5	5.4	5.4	5.2	5.4	5.5	5.5	5.5
Liquid, mg/L										
Ca		910	958	850	1,022	874	1,026	1,038	1,098	902
SO_3		387	415	421	649	371	594	548	512	460
SO_4		1,998	1,844	2,036	2,017	1,998	1,998	2,085	1,806	2,099
CO_3		90	162	144	162	158	189	195	216	270
Mg		144	110	120	89	186	163	192	197	194
Cl		369	404	326	284	461	432	755	1,010	496
Rel. sat., SO_3		1.0	3.2	2.4	4.1	1.4	3.8	4.1	4.1	3.2
Rel. sat., SO_4		1.2	1.1	1.1	1.3	1.1	1.2	1.2	1.1	1.1
Oxidation, %		97	95	98	100	99	99	97	83	99

Relative saturations were low for both $CaSO_3 \cdot 1/2H_2O$ and $CaSO_4 \cdot 2H_2O$, as shown in Table 9. The relative saturation of $CaSO_3 \cdot 1/2H_2O$ in the bleedstream for both the B-series and the C- and D-series of tests varied widely between unsaturated operation and a relative saturation in a few cases of about 5. There was no precise relationship of $CaSO_3 \cdot 1/2H_2O$ saturation and oxidation level. The relative saturation of $CaSO_4 \cdot 2H_2O$ was also generally low, reaching 1.3 in only two runs. In most cases the $CaSO_4 \cdot 2H_2O$ relative saturation, particularly in the C- and D-series of tests, was 0.9 to 1.1. $CaSO_4 \cdot 2H_2O$ unsaturated operation was, in fact, the rule in the C- and D-series two-tank oxidation. As with $CaSO_3 \cdot 1/2H_2O$ relative saturation, $CaSO_4 \cdot 2H_2O$ relative saturation showed no relationship to oxidation levels. Quantitative evaluations of relative saturations are discussed below.

SO_2 Removal

SO_2 removal efficiencies were generally in the range of 80% to 90% during the test program. There was no indication that forced oxidation affected SO_2 removal efficiency or that, conversely, SO_2 removal efficiency affected forced oxidation.

Air Stoichiometry

Excluding the B-1 and B-2 tests, stoichiometries of 1.4 to 2.8 (all air stoichiometries are expressed as lb atoms O/lb mole SO_2 absorbed) were investigated in the B-series of tests. The 0.4 to 0.8 air stoichiometries of the B-1 and B-2 series, which were limited by the original air metering system, were inadequate and produced at most about 60% oxidation. Tests with air stoichiometries of about 1.5 (B-2A, 5/8, 5/11, 5/16) produced about 60% to 80% oxidation. In other B-series tests, with air stoichiometries between 1.7 and 2.8, oxidation ranged from 72% to 99%. Within this range there was no precise relationship of oxidation efficiency to air stoichiometry or pH. There was a definite general trend of increasing oxidation efficiency with increasing air stoichiometry, however, as shown in Figure 15. Oxidation rates were definitely responsive to air stoichiometries but were also strongly influenced by other undefined factors.

Air stoichiometries in the C- and D-series of tests ranged from 1.6 to 2.8, with most in the range of 1.7 to 2.0. Lower air stoichiometries predominate because of the nature of the test procedure, which was to determine the minimum effective air rate. Again there was no precise relationship of oxidation efficiency to air stoichiometry or pH. In this case neither was there an evident trend of increasing oxidation efficiency with increasing air stoichiometry. As shown in Figure 16, air stoichiometries of 1.6 to 2.8 all produced oxidation levels of 99% or more, while the range 1.6 to 2.0 also produced oxidation levels between 90% and 95%. Above an air stoichiometry of 2.0 (excluding one unexplained aberrant run), however, all oxidation levels were above 95%. Oxidation levels approaching 100% were, in fact, easily attained over an appreciable range of air stoichiometries. Most or all of the oxidation occurred in the absorber hold tank. As was shown in Table 10, absorber bottoms (liquid draining from the absorber) oxidation level is the same, or nearly the same, as the bleedstream oxidation level.

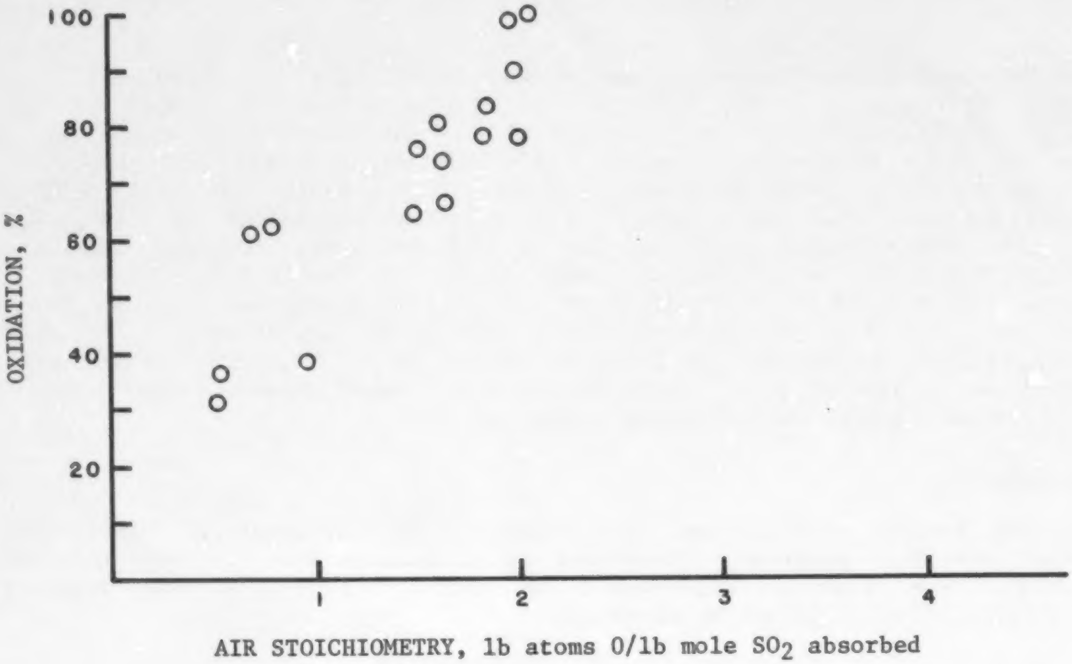


Figure 15. Percent oxidation versus air stoichiometry, venturi tank oxidation.

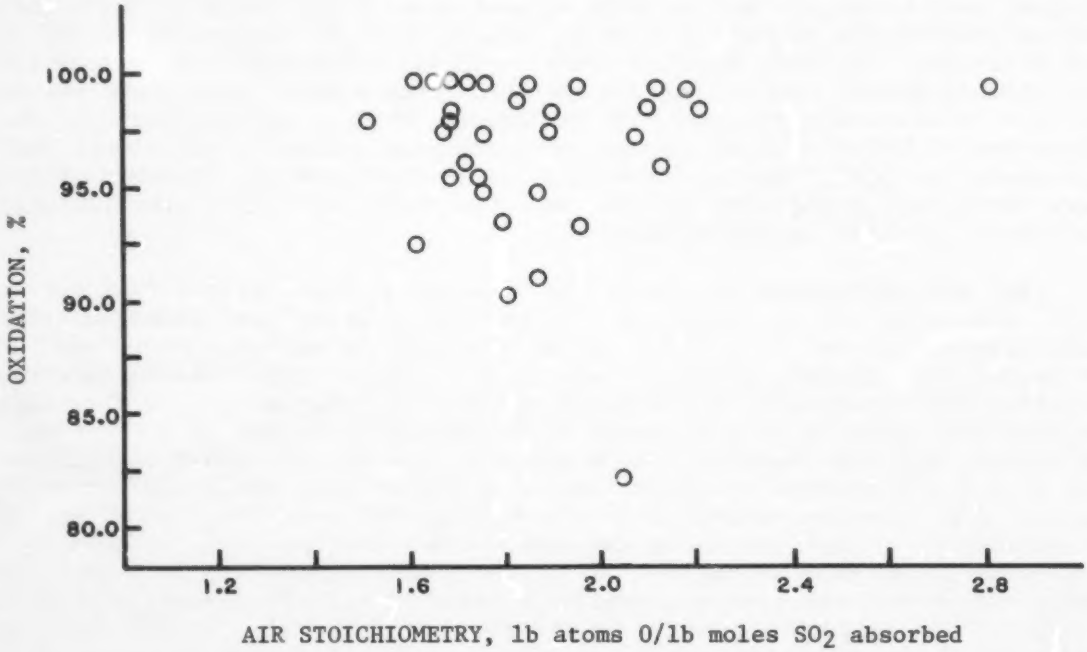


Figure 16. Percent oxidation versus air stoichiometry, two-tank oxidation.

Relative Saturation

In the background section, the source of sulfur (IV) species in solution and possible rate-limiting processes were discussed. Measured SO_3 and SO_4 concentrations in the absorber and bleedstream are an indication of the role of various dissolution and precipitation mechanisms in the overall oxidation process. Figure 17 shows $CaSO_4 \cdot 2H_2O$ relative saturation in the venturi hold tank. Figure 18 summarizes relative saturation of $CaSO_3 \cdot 1/2$ H_2O versus oxidation level for the B-series tests (oxidation only in the venturi hold tank) and C- and D-series tests (oxidation in both the venturi and absorber hold tanks).

The low levels of $CaSO_3 \cdot 1/2H_2O$ supersaturation in the B-series tests suggests that, as would be expected, dissolution of $CaSO_3 \cdot 1/2H_2O$ was occurring and that this mechanism was the source of HSO_3^- in solution. Dissolution was thus a potential, but not necessarily actual, rate-limiting mechanism. It should also be recognized that the relatively high pH of the venturi hold tank, a result of liquid carryover, undoubtedly contributed to a low dissolution rate and a corresponding depletion of sulfur (IV) species in solution. In contrast, the C- and D-series tests were characterized by relatively high levels of supersaturation at low oxidation levels, which decreased as the oxidation level increased and approached zero as the oxidation level approached 100%. This suggests that at least part of the HSO_3^- formed in the absorber was oxidized without being precipitated (11). At oxidation levels approaching 100% the relative saturation levels necessarily approached zero in both the B-series tests and the C- and D-series tests because of depletion of the sulfur (IV) species.

The relative saturation of $CaSO_4 \cdot 2H_2O$ is also an indication of a potential rate-limiting mechanism in the form of gypsum precipitation. As was shown in Table 9, the low, often less than one, $CaSO_4 \cdot 2H_2O$ relative saturations suggest no rate limitation due to $CaSO_4 \cdot 2H_2O$ crystallization. Either the high level of $CaSO_4 \cdot 2H_2O$ in the slurry or the high level of agitation energy (which serves to increase crystal area by both comminution and by inducing homogeneous nucleation) was apparently sufficient to maintain a low level of $CaSO_4 \cdot 2H_2O$ saturation.

Modeling Results

The results of the B-series tests and tests C-1 of the C-series tests were used by Combustion Engineering to calculate an overall mass-transfer coefficient, K_La, in the manner discussed in the background section. The K_La values were then used to calculate oxidation rates as described in the same section. The calculated oxidation rate is compared with the actual rate in Figure 19. The actual rate was calculated from mass balance data (the quantity of SO_2 removed, the measured oxidation level, and an assumed 20% natural oxidation level subtracted from the total oxidation level). The comparison also includes the Shawnee test facility tests. The comparison shows a fair agreement between the predicted and actual (calculated) values in most cases. A comparison of predicted air stoichiometries (developed from the same equations) with actual air stoichiometries, as shown in Figure 20, shows less agreement.

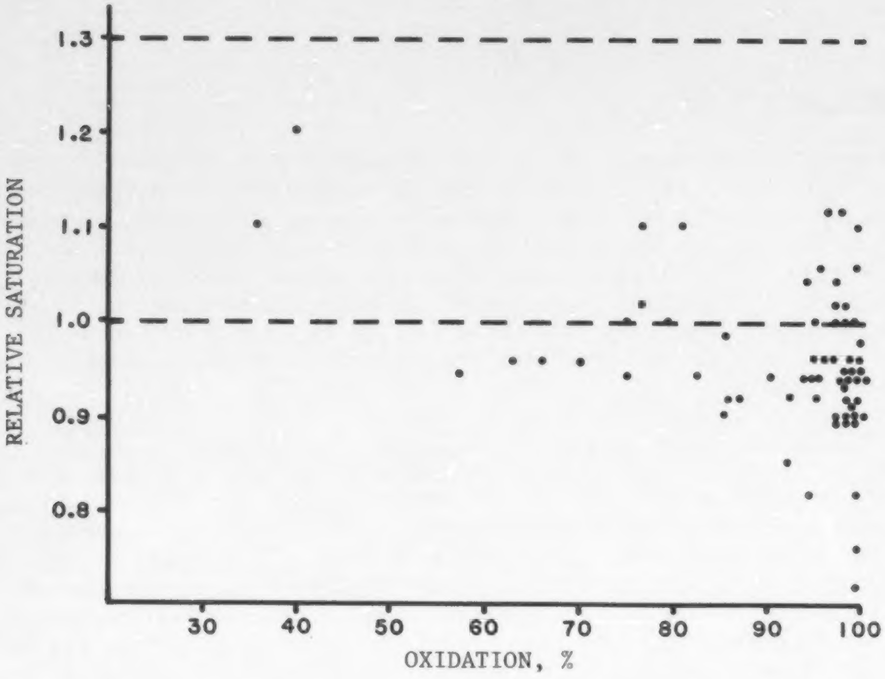


Figure 17. Relative saturation of $CaSO_4 \cdot 2H_2O$ in the venturi hold tank.

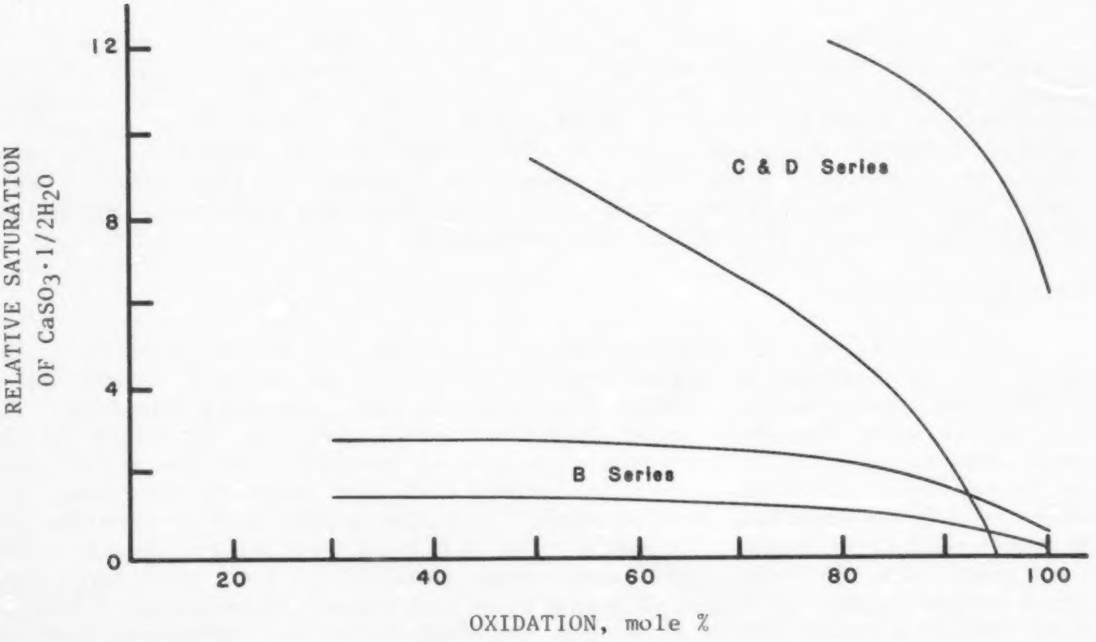


Figure 18. Relative sulfite saturation versus oxidation level.

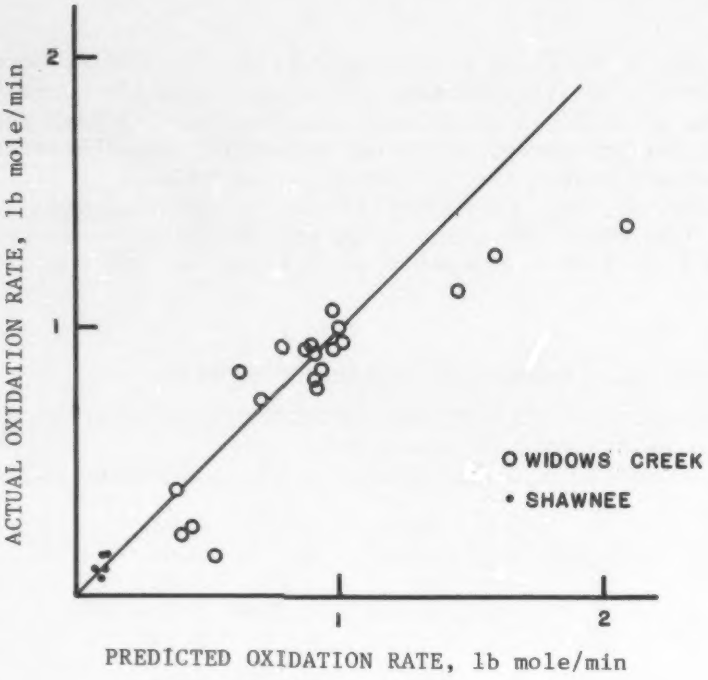


Figure 19. Comparison of actual and predicted oxidation rates.

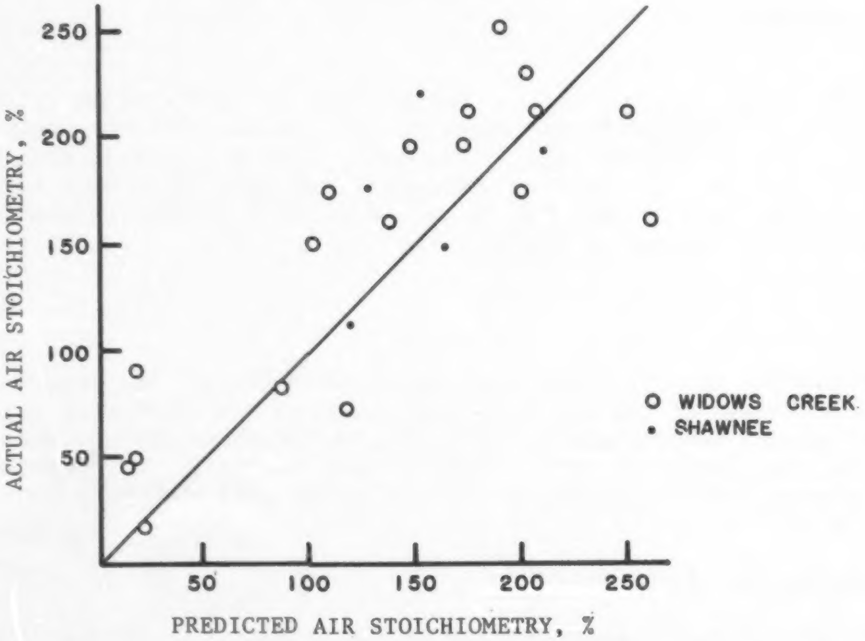


Figure 20. Comparison of actual and predicted air stoichiometries.

Radian (11) attempted to apply several models to the Widows Creek data. The models, representations of various mass-transfer- and oxidation-rate-based derivations, are shown in Table 11 along with the results of linear regression analyses. Oxygen partial pressures, oxidation rates, air stoichiometries, and mass-transfer coefficients were calculated from a mass balance of flue gas and air flows, SO_2 removals, and oxidation levels. Correlations are poor ($R^2 < 0.2$) except for the model in which both the dependent and independent variables were calculated from the same mass balance and are thus directly dependent.

TABLE 11. MODELS AND REGRESSION RESULTS

Model	Dependent variable	Independent variables	R^2	F-ratio	No. of observations
R = aS + b	R	S	0.134	4.95	34
R = aS^b	log(R)	log(S)	0.157	5.94	34
Ox = aS + b	Ox	S	0.001	0.03	34
R = a[K_ga x P_{O_2}] + b	R	[Kga x PO2]	0.9990	3.2×10^5	34
K_ga = aV + b	K_ga	V	0.105	3.73	34
K_ga = aV^b	log(K_ga)	log(V)	0.0705	2.43	34

R = reaction rate, a = interfacial area per unit volume, S = air stoichiometry, Ox = mole percent oxidation, Kg = gas-side oxygen mass-transfer coefficient, P_{O_2} = oxygen partial pressure, V = oxidation air superficial velocity, and b = fitted constant.

Oxidation rate and oxidation level show no correlation with air stoichiometry. The calculated K_ga shows no correlation with the superficial air velocity. The results do suggest, however, that an air stoichiometry of about 2 will produce 95% or more oxidation and that K_ga does not vary widely, suggesting that a K_ga of 8 to 12 x 10^{-6} lb-mol O_2/min-ft^3-psi O_2 represents typical operating conditions.

DEWATERING

The evaluation of the dewatering characteristics of the waste stream consisted of operation of the thickener-filtration system to dewater a portion of the waste stream and various tests to further characterize the dewatering properties of the waste slurry. These tests consisted of chemical and physical characterization of the solids, settling rate determinations, and filter leaf tests.

Chemical and Physical Properties

A comparison of compositions for the solids in Widows Creek unit 8 wastes produced with and without forced oxidation is shown in Table 12. Composite physical and chemical properties of oxidized waste are shown in Table 13. The

TABLE 12. TYPICAL COMPOSITIONS OF OXIDIZED AND UNOXIDIZED SOLIDS

	Wt % of solids
Typical Limestone FGD Waste	
$CaSO_3 \cdot 1/2H_2O$	31
$CaSO_4 \cdot 2H_2O$	24
$CaCO_3$	16
Limestone and fly ash inerts	28
Oxidized Limestone FGD Waste	
$CaSO_3 \cdot 1/2H_2O$	0.9
$CaSO_4 \cdot 2H_2O$	56
$CaCO_3$	14
Limestone and fly ash inerts	27

TABLE 13. PHYSICAL AND CHEMICAL PROPERTIES OF OXIDIZED SLUDGE

Oxidation, %	98
Solids, %	85
Ca/S ratio	1.46
Solids, mg/g	
$SO_3^=$	5.57
$SO_4^=$	312.0
$CO_3^=$	88.2
Ca^{++}	184.0
Mg^{++}	2.46
Inerts	274.0
Water	133.8

Average results of all runs ≥95% oxidation.

effects of these compositional differences are shown in scanning electron microscope photographs in Figure 21, which compares the crystal morphology of the wastes. About 80% of the small, platey crystals of $CaSO_3 \cdot 1/2H_2O$ that predominate in the unoxidized waste were smaller than 20 micrometers. In contrast, about 80% of the blocky $CaSO_4 \cdot 2H_2O$ crystals in the highly oxidized waste were between 20 and 100 micrometers. In both cases the size is represented by the major axis. (The spherical particles in the photographs are fly ash; the large irregular particles are, in all likelihood, limestone.)

The effect of the oxidation level on crystal morphology is further illustrated in Figure 22 showing photomicrographs of waste bleedstream solids at oxidation levels of 36%, 72%, and 99%. The increase in both the quantity and size of $CaSO_4 \cdot 2H_2O$ is obvious. The particle size distribution is further illustrated in Figure 23 showing the particle size distribution in wastes produced with and without forced oxidation. The size distribution was determined by visual microscopy.

Dewatering System Tests

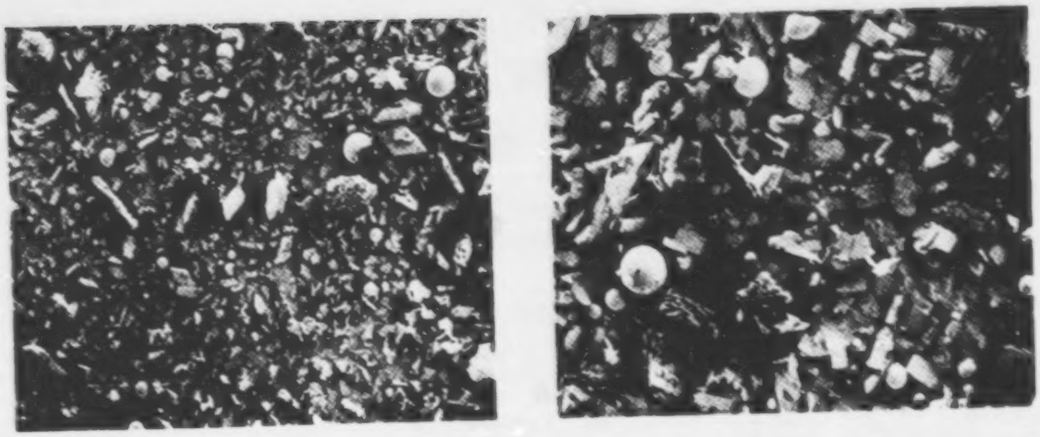
The dewatering system was designed to process waste slurry whose anticipated dewatering characteristics could be only generally estimated. Crystal morphology under actual operating conditions, the effects of fly ash and unreacted limestone, and the interactions of these slurry properties were largely indeterminable factors. The actual waste was so easily dewatered that the thickener and filter proved to be too large for the volume of waste obtainable in the sidestream from the FGD system effluent. Data in the more meaningful operating ranges near capacity rates could not be obtained.

The thickener was adequate for all flow rates and settling conditions. The overflow was always essentially free of solids; usually it contained less than 0.01% solids. The solids in the thickener underflow depended on the depth of the bed and the underflow rate and did not correlate with the laboratory settling rate data.

The filter was oversized and even at a low vacuum with one-third of the cloth area blinded with shellac, the maximum solids loading attainable was 50 to 70 $lb/hr\text{-}ft^2$, far below capacity. Figure 24 shows the relationship of filter cake solids to oxidation level for a number of B-series and C-series tests. Filter cake solids above 80% were usually attained at oxidation levels above 90%. At nearly complete oxidation levels, filter cake solids up to 90% were attained.

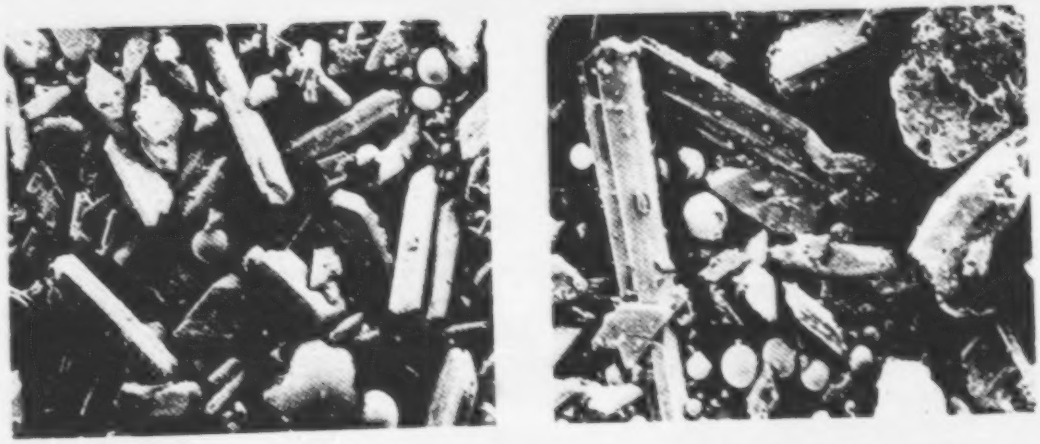
Settling Rate Tests

Laboratory settling rate tests were performed on a bleedstream sample at all steady-state conditions. The sample was poured into a one-liter graduated cylinder and the solids level (pulp volume) was recorded as a function of time to produce a settling curve as described in the background section. The time and distance to the point of compression were used to calculate the free settling rate. The data are shown in Table 14 for the B-series and early C-series tests. The settling rate as a function of oxidation level is shown in Figure 25 for the B-, C-, and D-series tests.



Unoxidized, 200x

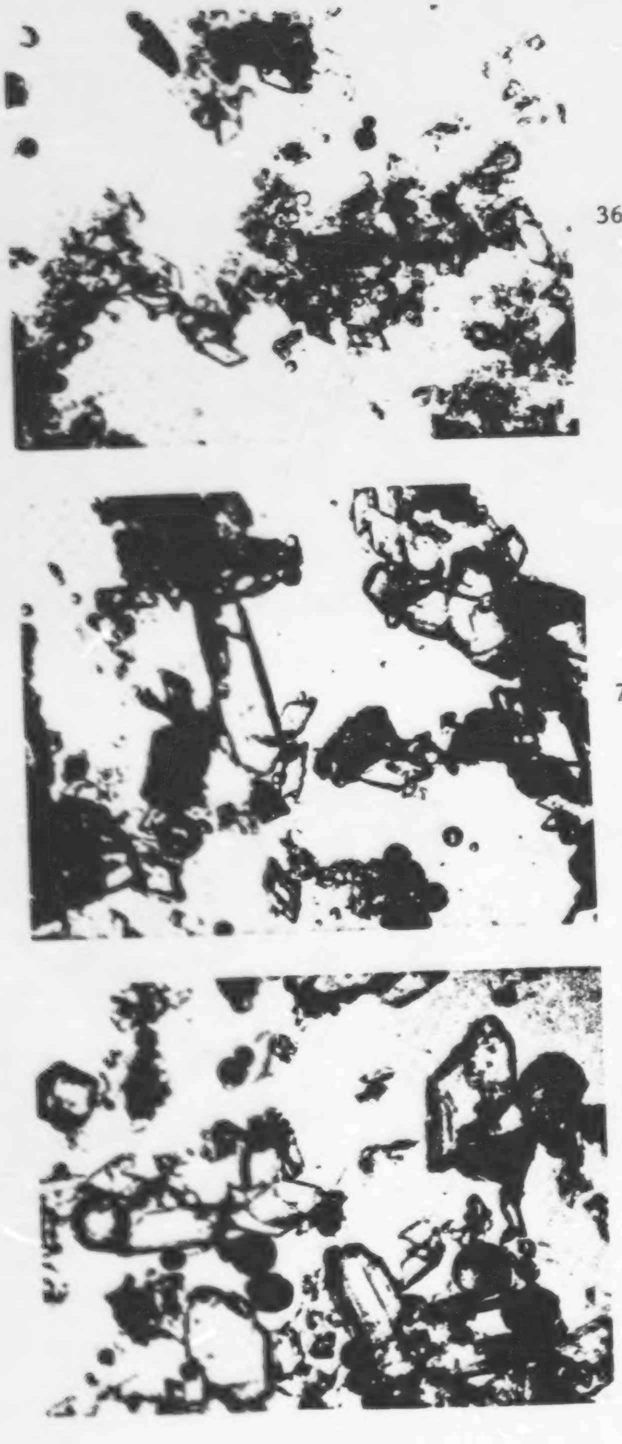
Unoxidized, 500x



Oxidized, 200x

Oxidized, 500x

Figure 21. SEM photographs of oxidized and unoxidized waste.


36% oxidation, 132x

72% oxidation, 132x

99% oxidation, 132x

Figure 22. Photomicrographs of waste at different oxidation levels.

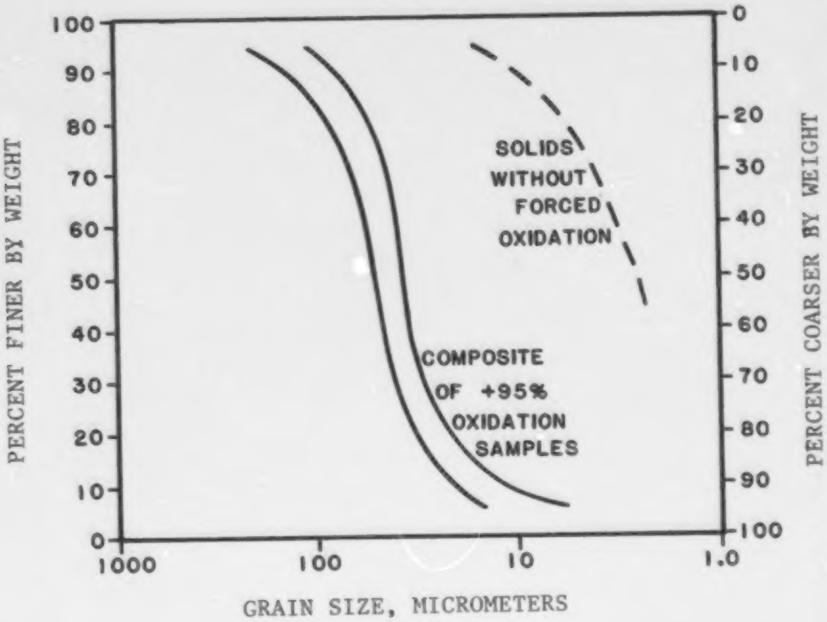


Figure 23. Particle size distribution of oxidized and unoxidized solids.

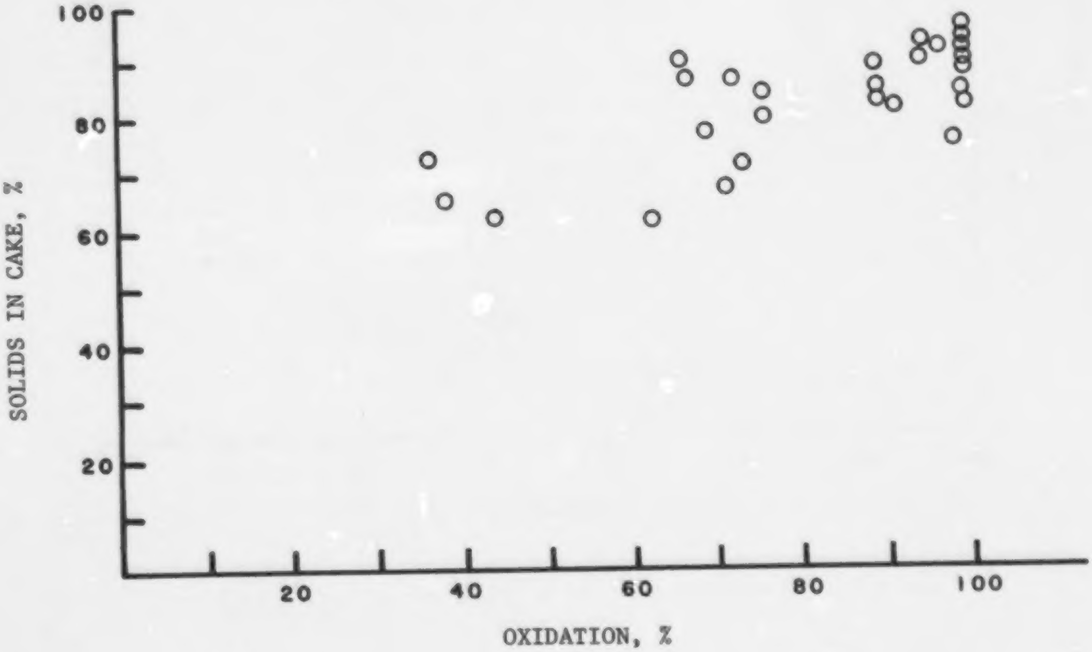


Figure 24. Relationship of rotary filter cake solids to oxidation level.

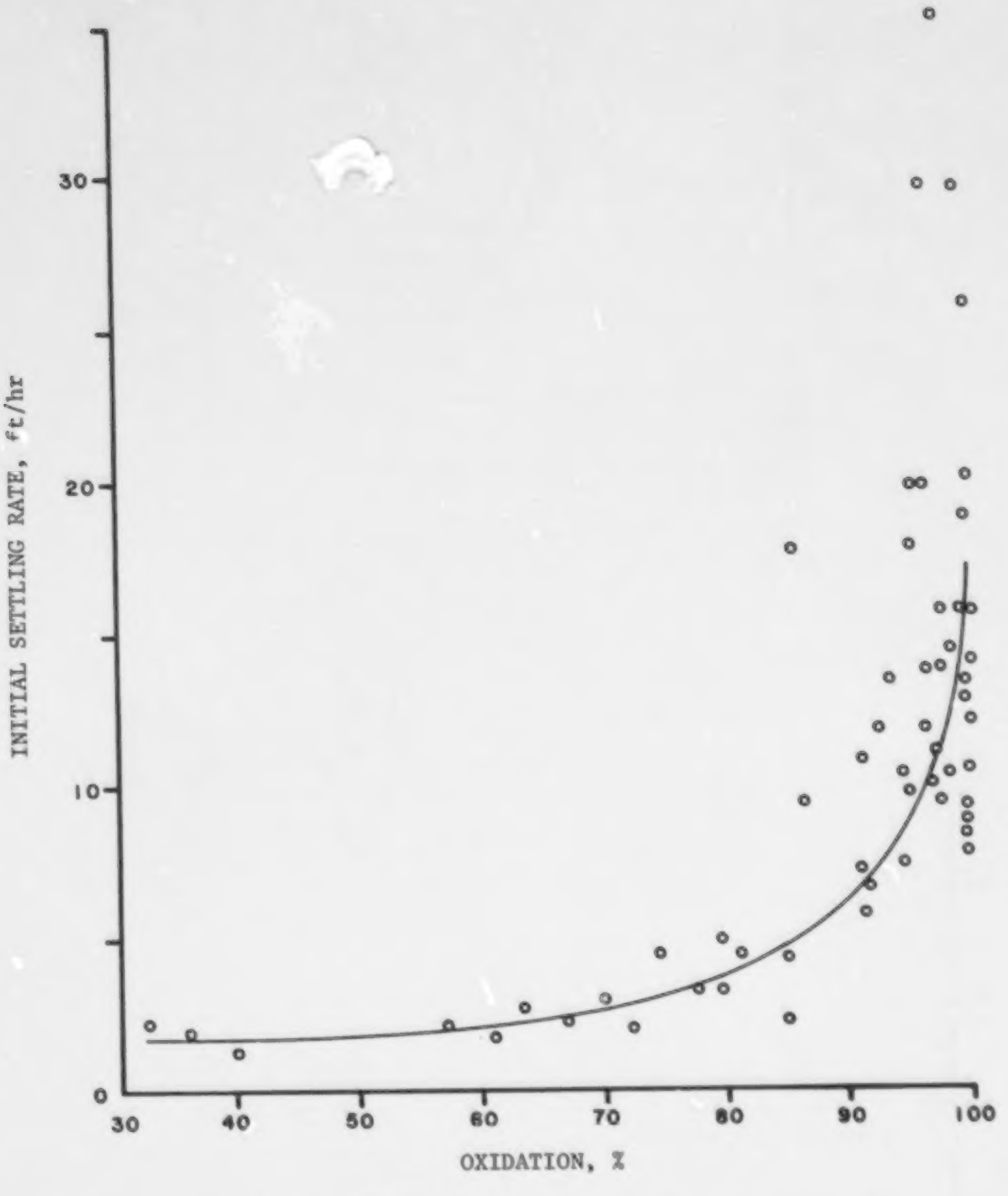


Figure 25. Settling rate as a function of oxidation level.

TABLE 14. LABORATORY SETTLING RATE DATA

Run	Date	Point of compression, min.	Settling rate, ft/hr	Slurry, % solids	% oxidation	Temperature of slurry, °F
B-1	4/20	70	0.5	12.7	40	115
B-1	4/22	40	1.0	5.3	32	115
B-1	4/23	40	0.9	9.0	36	115
B-2	4/30	40	0.9	11.7	61	111
B-2	5/1	30	1.4	8.6	63	100
B-2A	5/8	36	1.1	9.5	67	104
B-2A	5/11	22	2.1	11.2	81	117
B-2A	5/14	24	1.7	12.9	72	117
B-2A	5/15	19	1.9	18.5	85	109
B-2A	5/16	22	1.9	14.7	77	111
B-2	5/24	14	3.4	8.0	74	122
B-2	5/25	16	2.9	8.3	79	115
B-2	5/26	24	1.8	11.3	79	117
B-2B	5/31	15	3.4	11.0	91	118
B-2	6/1	10	5.5	8.9	99	118
C-1	6/27	10	5.7	9.3	99^{+}	124
C-1	6/29	9	6.8	9.8	99^{+}	122

The settling rate remained fairly low up to an oxidation level of about 80% to 90%. It then increased several fold between 90% and 100% oxidation. The wide variations in settling rate seen at the higher oxidation levels are partially experimental; the rapid settling rate (up to 6 in./min) precluded accurate visual determination of the solids level. Some variation is probably due to the variable limestone and fly ash content of the Widows Creek waste sludge. The results indicate that a thickener unit area requirement of about 2 ft^2/ton-day is necessary for thickening of highly oxidized sludge in the free settling area (up to about 40% solids).

Filter Leaf Tests

The filter leaf test apparatus and test procedure is described in Appendix B. Basically, the apparatus consists of a manually immersible 0.1 ft^2 filter apparatus with the same cloth as the rotary filter. By following a precise procedure of immersion and drying cycles, comparable data on rates, cake thickness, separability, and cake solids can be obtained. The procedure used simulated the rotary filter operating at 4 min/rev. with 38% submergence. A shortcoming of the test was that the vacuum was high and was not controlled. Cake formation rates may have been too high to be representative. On the other hand, the high vacuum simulated filtration conditions unattainable on the rotary filter because of the low vacuum necessarily used to accept the low input slurry flow rates from the thickener. This provided correlation of oxidation level versus dewatering characteristics at rotary filter operating conditions more typical of those in a well-designed system.

Filter leaf test data on the B-series and early C-series tests are shown in Table 15 and Figure 26. In all cases the higher solids thickener underflow produced a thicker, higher solids filter cake. The thicker cake indicates that flow resistance in the cake was not a limiting factor under the conditions of the test. The cause of the higher solids content with the higher-solids thickener underflow is less evident but it may have been the result of the effects of the pressure differential and pressure gradient on cake density and crystal texture. The relationship of cake solids to the oxidation level shown in Figure 26 is similar to the rotary filter results. In general, cake solids over 80% were attained at oxidation levels over 90%.

A comparison of the filter leaf test results with the rotary filter results is shown in Table 16. In most cases the cake solids are in good agreement although the filter leaf test cakes were usually about twice as thick as the rotary filter cakes. The general agreement of the two data sets encourages confidence in laboratory tests as an indication of actual filter performance.

TABLE 16. COMPARISON OF VACUUM FILTER DATA AND FILTER LEAF TEST DATA

	Rotary filter data		Filter leaf test data	
Test No.	Solids, %	Average cake thickness, in.	Solids, %	Cake thickness, in.
B-1	61.2	3/4	61.5	1-3/4
B-1	70	7/16	61.7	3/4
B-1	65	3/8	63.1	3/4
B-2	68.1	3/4	69.6	7/8
B-2	67.6	7/8	69.6	1-1/8
B-2	71.3	3/4	51.0	3/4
B-2	73.8	3/4	73.2	1-5/8
B-2	78.5	7/8	72.8	7/8
B-2	75.4	3/8 (avg)	64.2	1/8
B-2	76.5	5/8 (avg)	68.2	2-3/8
B-2	79.5	5/8 (avg)	72.2	1-3/16
B-2	69.8	1 (avg)	70.9	5/8
B-2	68.9	3/4 (avg)	70.6	1
C-1	81.9	5/8	75.7	5/8
C-1	83.9	9/16	84.7	1-1/8

TABLE 15. FILTER TEST LEAF DATA

Test condition	Sample location	Solids, %	Oxidation, %	pH	Filter cake solids, %	Filter cake thickness, in.	Filter cake ease of separation[a]
B-1	Feed	12.7	37	5.7	54	3/4	Good
	Underflow	31.3	48	6.0	61	1-3/4	Good
B-1	Feed	5.3	32	5.5	49	1/4	O.K.
	Underflow	20.4	24	6.0	61	1-3/4	O.K.
B-1	Feed	9.0	35	5.5	54	3/8	O.K.
	Underflow	19.3	38	6.1	63	3/4	Good
B-2	Feed		62	5.9	61	3/8	Good
	Underflow		63	6.6	70	7/8	Good
B-2	Feed	8.6	62	5.8	60	3/8	Good
	Underflow	32.3	74	6.3	70	1-1/8	Good
B-2	Feed	9.6	67	5.6	56	3/8	Good
	Underflow	20.7	75	5.9	51	3/4	Good
B-2	Feed	8.9	98	5.6	46	3/4	Good
	Underflow	17.8	99+	5.6	73	1-5/8	Good
B-2	Feed	11.2	81	5.4	63	1/4	Good
	Underflow	35.7	78	6.0	73	7/8	Good
B-2	Feed	12.9	72	5.5	59	5/16	Good
	Underflow	1.9	72	5.6	64	7/8	Good
B-2	Feed	18.5	86	5.4	60	3/8	Good
	Underflow	26.8	80	6.0	69	2-3/8	Good
B-2	Feed	14.7	77	5.8	60	5/16	Good
	Underflow	28.9	77	6.0	69	2-3/8	Good
B-2	Feed	8.2	75	5.7	55	3/16	Good
	Underflow	22.0	77	9.2	70	5/8	Good
B-2	Feed	11.3	79	5.7	57	1/4	Good
	Underflow	31.7	84	6.5	71	1	Good
B-2	Feed	10.5	91	5.5	63	1/4	Good
	Underflow	25.9	90	6.5	74	1/2	Good
B-2	Feed	8.9	99+	5.3	78	1/4	Good
	Underflow	17.8	99+	6.0	82	3/8	Good
C-1	Feed	9.0	99	5.7	74	1/8	Fair
	Underflow	14.4	100	6.3	76	5/8	Fair
C-1	Feed	9.8	99+	5.6	85	1/8	Fair
	Underflow	31.6	99+	6.4	85	1-1/8	Fair

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[a] Based on observation: good indicates relatively easy separation, fair indicates minor sticking or some difficulty of separation.

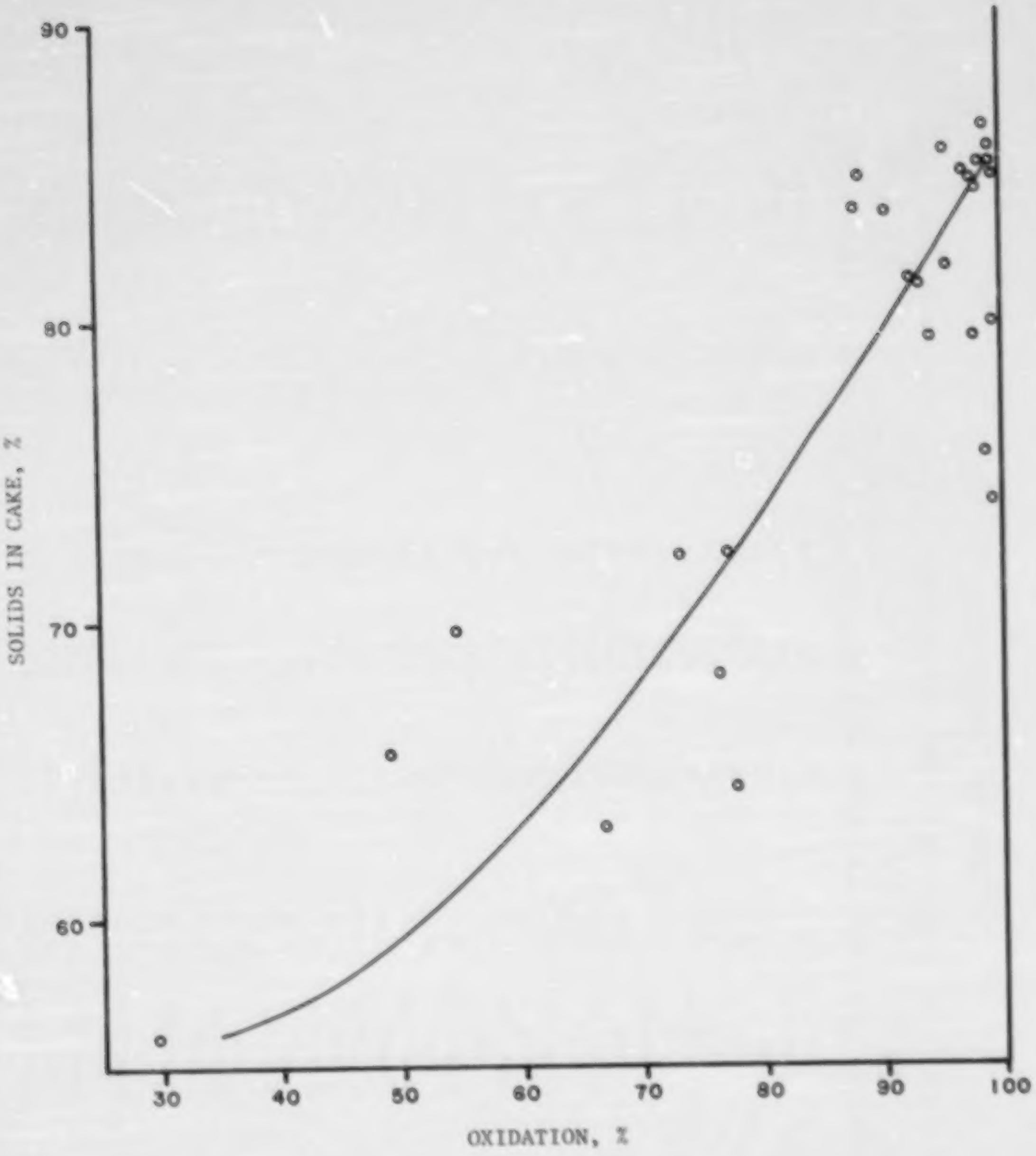

Figure 26. Relationship of filter leaf test cake solids to oxidation level.

CONCLUSIONS

Forced oxidation to levels approaching 100% is possible in the Widows Creek unit 8 FGD system by addition of higher power agitators and an air sparging system. Oxidation in both the absorber and venturi hold tanks with a total air stoichiometry of 2 lb atoms O/lb mol SO_2 absorbed, or more, will consistently produce over 95% oxidation to gypsum at the boiler operating conditions prevailing during the test period without affecting SO_2 removal or operational performance. The oxidized waste produced can be consistently dewatered to 80% solids or more in conventional equipment and can be handled by conventional solids handling equipment such as conveyors and trucks.

The venturi hold tank oxidation mode was compromised by the particular configuration of the Widows Creek unit 8 system, which permitted a large liquid entrainment from the venturi to the absorber. The resulting mixing of the absorbent in the two liquid loops precluded true separation of the two liquid systems essential to efficient oxidation. It is possible that gas flow vanes or mist collectors between the venturi or absorber could reduce the carryover, thus improving oxidation efficiency in this mode.

Gypsum relative saturation was near 1.0 during most of the tests with oxidation in both hold tanks. This low saturation level is in agreement with data from other forced-oxidation tests. It is attributed to the presence of abundant seed crystals (33). Forced oxidation, therefore, should not affect scaling, since gypsum supersaturation levels of 1.3 to 1.4 are normally necessary to initiate rapid nucleation that causes scaling (14).

The thickener and rotary filter were oversized for the dewatering characteristics of the waste slurry at oxidation levels over about 90%. The system was operated too far below capacity to provide decisive design and scale-up data. At oxidation levels above 95% the system consistently produced waste solids above 80%. Laboratory filtration tests produced results similar to the rotary filter results in terms of dewatering characteristics and oxidation level. Based on the laboratory tests, the thickener requirements are a minimum 1.7 ft^2/ton-day and the filter requirements are about 200 lb/ft^2-hr.

The crystal size of the highly oxidized waste was primarily in the 20 to 100 micrometer range, whereas the crystal size of the waste produced without forced oxidation was primarily below 20 micrometers.

Laboratory tests of the oxidized waste indicated that the free settling rate of the waste increased little until about 90% oxidation was reached and that it then increased rapidly as the oxidation level increased from 90% to 100%. Above a 95% oxidation level laboratory settling rates were usually 20 to 30 ft/hr.

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APPENDIX A

FORCED-OXIDATION EQUIPMENT LIST

Absorber Hold Tank Assembly

Diameter - 33 feet
Overall Height - 27 feet

1. Motor (1): 300 hp, 1,750 rpm, 460 V, 60 cycle, 3 phase.
2. Shaft (1): Steel, 22 ft from base, welded coupling.
3. Impeller (1): Type R321, 6 blades, 88 in. diameter, 68 rpm.
4. Baffles (4): 33 in. wide, 6 in. off wall, 90° spacing, full length.
5. Mixer mounting data : Unit size 735, vertical downward load 37,000 lb, torque 525,400 in.-lb, bending moment 2,147,000 in.-lb.

Venturi Hold Tank

Diameter - 18 feet
Overall Height - 25 feet

1. Agitator motor (1): 75 hp, 1,750 rpm, 460 V, 60 cycle, 3 phase.
2. Shaft (1): Steel, 20 ft 2 in. from base.
3. Impeller (1): Type R321, 6 blades, 78 in. diameter.
4. Baffles (4): 18 in. wide, 4 in. off wall, 90° spacing, full length.

Reslurry Tank

Diameter - 7 feet
Overall Height - 10 feet

1. Agitator motor (1): 10 hp, 460 V, 60 cycle, 3 phase.
2. Agitator shaft (1): 3 in. diameter, 104 in. long.
3. Impeller (1): 4 blades, 50 in. diameter.
4. Baffles (4): 6 in. wide, 2 in. off wall, full length.

Pump Motors

1. Bleed pump motors (2): 2 hp, 1,730 rpm, 230/460 V, 6.4/3.2 A, 60 cycle, 3 phase.
2. Thickener underflow pump motors (2): 5 hp, 230/460 V, 16.4/8.2 A, 60 cycle, 3 phase, 54-430 rpm, Varidrive type VAV-TF-60.

3. Reslurry transfer pump motors (2): 2 hp, 230/460 V, 6.4/3.2 A, 60 cycle.

4. Filtrate pump motor (4): 3 hp, 230/460 V, 60 cycle, 3 phase.

5. Vacuum pump motor (4): 20 hp, 230/460 V, 60 cycle, 3 phase.

6. Vacuum filter drum motor (4): 0.5 hp, 230/460 V, 60 cycle, 3 phase, 66-7 rpm gear drive.

7. Vacuum filter agitator motor (4): 0.5 hp, 230/460 V, 60 cycle, 3 phase, 538-2150 gear drive.

8. Flocculent feeder drive motor (1): 0.3 hp, 115 V, 60 cycle, 1 phase.

9. Flocculent mixer motor (1): 0.3 hp, 115/230 V, 60 cycle, 1 phase.

10. Flocculent metering pump motor (1): 0.25 hp, 115 V, 60 cycle, 1 phase.

11. Thickener agitator motor (1): 0.5 hp, 230/460 V, 60 cycle, 3 phase, 60:1 drive ratio.

12. Reslurry agitator motor (1): 10 hp, 230/460 V, 60 cycle, 3 phase, 31:1 drive ratio, 56 rpm.

Pumps

1. Bleed pumps (2): Centrifugal, size 2/1.5.

2. Thickener underflow pumps (2): Centrifugal.

3. Reslurry transfer pumps (2): Centrifugal, size 2/1.5.

4. Vacuum pump (1): 257 ft3/min at 20 in. Hg.

5. Filtrate pump (1): 50 gal/min, size 1 - 1 1/2 - 8, STD No. ST, material construction: CD4 MCU, impeller diameter 8 in.

6. Flocculent transfer pump (1)

7. Flocculent metering pump (1): Discharge pressure 50 psig (max).

Vacuum Filter Assembly

1. Standard universal drum rotary vacuum filter (1): 4 ft 6 in. diameter, 6 ft face, 84.8 ft^2 effective filtration area, carbon steel, 1/4 in. carbon steel knife apron assembly with polypropylene blade, 3 in. nozzle spacing, Dacron cloth.

2. Discharge blower (1): Cyclonair model with base, 5 hp, 230/460 V, 60 cycle, 3 phase, 92 in. H_2O suction, 111 in. H_2O pressure, 160 ft^3/min at 2 psi.

Portable Compressors

1. Ingersoll-Rand Model DXL1200 (10): Single-stage screw type, 1,200 ft^3/min at 125 psi.

Instrumentation

1. Current output controller
2. Recorders
3. Magnetic flowmeters: underflow (2), bleedstream (2)
4. Differential pressure transmitter (1)
5. Motor control center (1)
6. Positioner (1)
7. Cylinder actuator (1)
8. Nuclear density meters (2)
9. Air flow transmitter (venturi and absorber) (1)

APPENDIX B

CHEMICAL ANALYSIS PROCEDURES

ANALYTICAL METHODS

The following section contains a description of the preparation and analysis techniques used for all samples. Table B-1 summarizes the analyses required at each of the five sample points.

AQUEOUS-PHASE SAMPLE PREPARATION

The liquid-phase samples collected required special preservation techniques to prevent degradation of samples and to insure that the sample analyzed was representative of species actually present in the system. All sample bottles for liquid-phase cation and anion analyses contained a measured amount of deionized water and hydrogen peroxide. Deionized water diluted the sample to prevent additional precipitation if supersaturated species were present. Hydrogen peroxide was added to the bottle to convert any liquid sulfite species to sulfate. This eliminated interference by sulfite during analysis.

Liquid sulfite samples were taken in bottles containing a known concentration of iodine in a sodium acetate-acetic acid buffered solution.

Aqueous carbonate samples were also taken from the filtered liquid. The samples were preserved in an ammonium hydroxide-disodium EDTA buffered solution which maintained a pH of 10.

SOLID-PHASE SAMPLE PREPARATION

A portion of the dried solids was dissolved for species analyses and to determine the acid insoluble portion. This procedure involved adding a weighed quantity of solids to a volumetric flask half filled with deionized water. Sufficient hydrochloric acid was added to reduce the pH to 2.

The solution was stirred vigorously for 30 minutes then brought up to volume in the volumetric flask and filtered through a weighed filter paper. Solids remaining in the volumetric flask were quantitatively transferred to the filter by several small washings with deionized water. The filter paper was oven dried and then reweighed to determine the acid insoluble portion of the solids (ash). A portion of the filtrate from the filtration step was retained for anion and cation analyses.

TABLE B-1. SUMMARY OF ANALYSES

Sample phase	51 Bleedstream	52 Thickener underflow	53 Thickener Overflow	54 Vacuum filter drum	55 Absorber bottoms
Liquid	$SO_3^=$, $SO_4^=$, NO_3^-, Cl^-, $CO_3^=$ Anions Ca^{++}, Mg^{++}, Na^+, K^+, NH_4^+ Cations				$SO_3^=$, $SO_4^=$, NO_3^-, Cl^-, $CO_3^=$ Anions Ca^{++}, Mg^{++}, Na^+, K^+, NH_4^+ Cations
Solid	$SO_3^=$, $SO_4^=$, $CO_3^=$ Anions Ca^{++}, Mg^{++} Cations Acid insoluble quantity Wt % solids	$SO_3^=$, $SO_4^=$, $CO_3^=$ Anions Ca^{++}, Mg^{++} Cations Acid insoluble quantity Particle size distribution Wt % solids	% solids	% solids Thickness on drums	$SO_3^=$, $SO_4^=$, $CO_3^=$ Anions Ca^{++}, Mg^{++} Cations Acid insoluble quantity Wt % solids
Slurry	pH Temperature Settling rate test	pH Temperature Filter leaf test	pH Temperature		pH Temperature

CATION ANALYSES

Analyses for calcium, magnesium, sodium, and potassium were done by atomic absorption spectrophotometry. In this technique, the aqueous sample is aspirated into a flame where the various cations are converted to their elemental state. For each element analyzed, a special emission source lamp produces a beam of light that is passed through the flame. The frequency of the beam is such that the elemental state of the species to be determined will absorb some of the beam energy in direct portion to its concentration. By comparing this absorptance with the absorptances of a number of standards, the concentration of the element in the unknown solution may be determined.

ANION ANALYSES

An ion chromatograph was used to determine the concentration of chloride and sulfate. In this method the samples are diluted to the appropriate concentration ranges and aliquots are injected into the instrument for separation in an ion exchange column. Changes in the conductivity of the effluent stream due to chloride and sulfate ions were compared with those of standard solutions which bracket actual concentrations. Both species can usually be measured in one injection. The accuracy limits are typically better than ±5%.

An iodine back-titration technique was used to determine sulfite. In this method, excess iodine is added to an aliquot of the sample and the unreacted iodine is measured by titrating with a standardized thiosulfate solution. The sulfite in the sample is then obtained by difference from the quantity of iodine originally added and the amount determined by the thiosulfate titration.

The aqueous CO_2 concentrations were determined by means of a nondispersive IR analyzer. To briefly describe the technique, a known volume of sample is injected into an acid pool reactor at pH 2.5. CO_2 is liberated from the buffered sample and carried by a nitrogen gas purge stream through a drying medium to remove water vapor. The dried CO_2 next passes into an IR detector cell, where the amount of CO_2 present is monitored. A recorder equipped with a disc-chart integrator is used to measure the peak area. Standards of known CO_2 concentrations that bracket sample values are also analyzed for comparison. The peak areas, standard concentrations, volume of sample injected, peak area of samples, and amount of buffer used to preserve each sample are used as inputs into Radian's CO_2 computer program. The program performs a modified linear least squares regression analysis to calculate concentrations of CO_2 in millimoles per liter.

WEIGHT PERCENT SOLIDS

Weighed volumetric flasks were filled with slurry to the calibration mark at each sample location. The filled flasks were reweighed, then the contents were filtered through a weighed filter paper. The filter paper was oven dried and then reweighed to determine the weight percent solids of the slurry.

pH

A portable pH meter electrode was calibrated by use of standard buffer solutions of pH 7.0 and pH 5.0. The standardized pH meter electrode was then immersed in the slurry flowing out of each sample location. The temperature of the slurry was measured and temperature compensation control on the meter set. The meter was then turned from the standby to the measuring mode, and the pH was read.

TEMPERATURE

The temperature of each sample was determined by immersing the bulb of a Celsius mercury thermometer in the flowing slurry at each sample point.

DRUM FILTER CAKE

A 2 to 4 inch square piece of solids was removed from the vacuum filter drum just ahead of the discharge scrapers. The solid cake was taken to the lab where its thickness was measured to the nearest 1/16 of an inch. The cake was then weighed on a top-load balance and oven dried. After drying, the cake was reweighed to determine the percent solids in the cake.

FILTER LEAF TESTS

Filter leaf tests, designed to simulate the plant vacuum filter, were performed on the thickener underflow (Point 52). A standard filter leaf apparatus was supplied by Komline-Sanderson. The apparatus contained 0.1 ft of filter surface area, with the same cloth type used in the vacuum filter. The filter leaf test configuration used is illustrated in Figure B-1. The filter was immersed in a well-stirred bucket of slurry, with vacuum applied, for one and half minutes, then removed while still under vacuum and allowed to dry for two minutes. This simulated a drum filter speed of 4 minutes per revolution, at 38% drum submergence. The filter cake thickness, ease of separability from the filter, and weight percent solids were all determined and recorded. The volume and clarity of filtrate were also recorded.

PARTICLE SETTLING TEST

The particle settling test was performed on the thickener underflow to determine how well particles were settling in the thickener. The plastic pail sample from the thickener was stirred vigorously to assure uniformity of the slurry and then rapidly poured into a one-liter graduate cylinder. A graph of time versus total distance settled was then plotted to determine the point of compression of the solids.

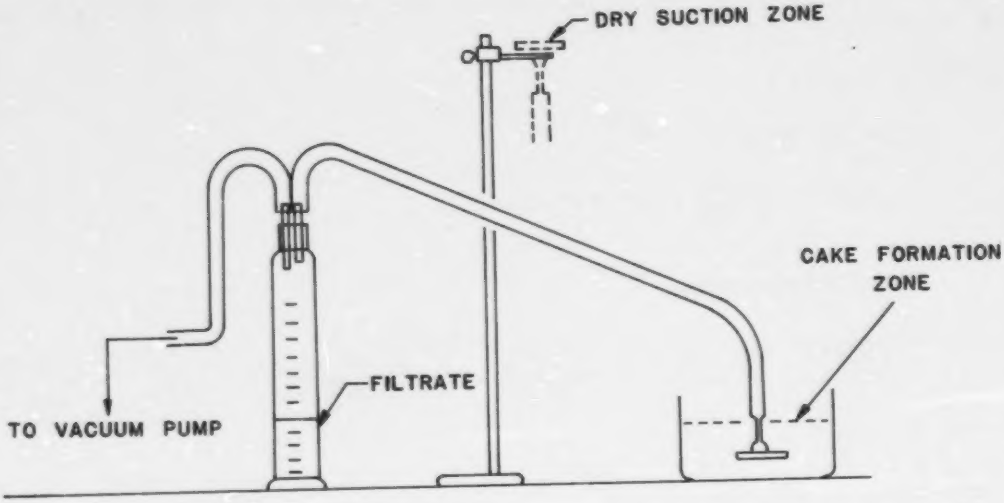

Figure B-1. Filter leaf test apparatus.

SAMPLE CALCULATION

Following is an example of the daily data work-up performed on the operating and analytical data recorded during testing.

First, operating data from several data sheets were averaged over the 24-hour period. Oxidizing air data were taken from the assistant unit operator's oxidation unit log, and boiler and scrubber data were taken from the scrubber operator's control room log.

Boiler load	290 MW
ID fan current	470 A
SO_2 in	1,700 ppm
SO_2 out	Instr. out
ΔSO_2 (use shift chemist readings)	1,572 ppm
LS feed rate	41.8 gal/min
LS solids	43.7%
Oxidation air flow	3,000 aft^3/min
Oxidation air temperature	120°F

In this case, the outlet SO_2 instrument was down, and ΔSO_2 was estimated from the shift chemist's wet-method SO_2 readings.

Second, SO_2 removal rates and oxygen and calcium feed rates were estimated based on the flow rate data:

SO_2 Pickup Rate

Flue Gas Rate -

$$346{,}900 \times \frac{470}{500} = 326{,}000 \text{ sft}^3\text{/min}$$

SO_2 Absorption Rate -

$$\frac{326{,}000 \text{ sft}^3\text{/min}}{379 \text{ sft}^3\text{/lb-mole}} \times 1{,}573 \times 10^{-6} \frac{\text{lb-mole } SO_2}{\text{lb-mole gas}} = 1.35 \frac{\text{lb-mole } SO_2}{\text{min}}$$

The flue gas rate calculated above was based on the most recent velocity traverse, 346,900 sft^3/min at 500 amps, and adjusted at 470 amps.

Ca Feed Rate

LS Solids Feed Rate

$$0.437 \times 41.8 \text{ gal/min} \times (8.34 \times 1.357 \text{ lb/gal}) = 207 \frac{\text{lb solids}}{\text{min}}$$

Ca Molar Feed Rate

$$\frac{207 \text{ lb}}{\text{min}} \times \frac{0.9 \text{ lb } CaCO_3}{\text{lb solids}} \times \frac{1 \text{ lb-mole Ca}}{100 \text{ lb } CaCO_3} = 1.86 \frac{\text{lb-mole Ca}}{\text{min}}$$

Oxygen Feed Rate

Orifice Temperature Correction

$$3{,}000 \text{ aft}^3\text{/min} \times \left(\frac{460 + 120}{460 + 160}\right)^{1/2} = 2{,}902 \text{ aft}^3\text{/min, } 120°F$$

(The orifice is calibrated at 160°F)

Standard Conditions (60°F)

$$2{,}902 \times \left(\frac{460 + 60}{460 + 120}\right) = 2{,}601 \text{ sft}^3\text{/min}$$

Oxygen Molar Rate

$$\frac{2{,}601 \text{ sft}^3\text{/min}}{379 \text{ sft}^3\text{/lb-mole}} \times \frac{.209 \ O_2}{1 \text{ air}} \times \frac{2 \ O}{1 \ O_2} = 2.87 \text{ lb-atoms/min}$$

Third, calcium-to-sulfur and oxygen-to-sulfur ratios were calculated based on these values.

Stoichiometries

$O/SO_2 = 2.87/1.35 = 2.1$

$Ca/SO_2 = 1.86/1.35 = 1.4$

Fourth, a table of analysis results was prepared. This involves three stages of calculations.

1. Solid and liquid concentrations in the thickener feed slurry were calculated.
2. To put solid and liquid phase concentrations on a whole-slurry basis, the analysis results were adjusted for solid and liquid concentrations in the slurry. The following example is for a single chemical species, SO_3^{2-}.
3. The calculated results were summed and entered in the table, along with oxidation and calcium stoichiometry.

Thickener Feed Slurry Properties (Stage 1)

Slurry Density 1,014 g/L
Wt. Frac. Solids 2.49%
Solids Concentration = .0249 x 1,014 = 25.25 g/L slurry
Clear Liquid Concentration

$$(1-.0249) \times 1.014 = 0.989 \frac{\text{L clear liquid}}{\text{L slurry}}$$

Sample Calculations for SO_3^{2-} (Stage 2)

Liquid phase:

$$10.8 \frac{\text{mmole}}{\text{L liquid}} \times 0.989 \frac{\text{L liquid}}{\text{L slurry}} = 10.7 \frac{\text{mmole } SO_3^{2-}}{\text{L slurry}}$$

Solid phase:

$$0.161 \frac{\text{mmole}}{\text{g solid}} \times 25.25 \frac{\text{g solid}}{\text{L slurry}} = 4.07 \frac{\text{mmole } SO_3^{=}}{\text{L slurry}}$$

Total in slurry, solid + liquid: $10.7 + 4.07 = 14.8 \frac{\text{mmole}}{\text{L slurry}}$

ANALYSIS RESULTS TABLE (Stage 3)

	Thickener feed					Underflow (52)
	Liquor		Solids		Slurry	Solids
		Slurry basis		Slurry basis		
	mmole/L (analysis)	$\frac{\text{mmole}}{\text{L slurry}}$	mmole/g (analysis)	$\frac{\text{mmole}}{\text{L slurry}}$	mmole/L	mmole/g (analysis)
$SO_3^=$	10.8	10.7	0.161	4.07	14.8	0.108
$SO_4^=$	17.2	17.0	2.11	53.3	70.3	1.73
Ca^{++}	26.4	26.1	4.22	107.	133.1	5.16
Oxidation	61.4		92.9		82.6	94.1
Ca/S			1.86		1.56	

Finally, a summary table of these results was prepared.

Summary 0900 10-27 → 0900 10-28

Removal	92.5%
Oxidation	
Feed solids	92.9%
Underflow solids	94.1%
Filter cake % solids	84
Boiler load	290 MW
SO_2 molar abs. rate	1.35 $\frac{\text{lb-mmole}}{\text{min}}$
O/SO_2	2.1
Ca/S	
Analysis basis	1.56
Flow basis	1.4

APPENDIX C

CHEMICAL ANALYSIS RESULTS

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TABLE C-1. ACTUAL OPERATING CONDITIONS

Date	Test	Flue gas flow rate, ksft^3/min at 1 atm, 60°F	Inlet SO_2, ppm	Outlet SO_2, ppm	$CaCO_3$ stoichiometry	Venturi solids, %	Air stoichiometry, atoms O/mole SO_2
4/20/79	B-1	250	1,340	210	1.4	13.3	0.8
4/22/79	B-1	210	1,840	350	1.2	8.4	0.4
4/23/79	B-1	220	1,670	290	1.6	8.1	0.7
4/30/79	B-2	260	1,700	440	1.3	9.2	0.7
5/01/79	B-2	270	1,620	400	1.2	13.8	0.8
5/08/79	B-2	300	2,010	430	1.2	14.4	1.5
5/10/79	B-2	245	1,650	130	1.2	6.9	2.8
5/11/79	B-2	320	1,850	390	1.1	12.1	1.5
5/14/79	B-2	320	1,900	490	1.3	12.0	2.1
5/15/79	B-2	300	1,840	350	1.3	14.2	1.7
5/16/79	B-2	305	1,870	400	1.2	14.6	1.4
5/24/79	B-2	300	1,810	610	1.2	10.0	1.7
5/25/79	B-2	280	1,540	360	1.2	10.9	1.7
5/26/79	B-2	260	1,890	350	1.1	11.2	2.1
5/31/79	B-2	270	1,930	400	1.2	10.1	2.4
6/01/79	B-2	270	2,380	520	1.1	13.2	2.0
6/29/79	C-1	390	1,900	320	1.4	9	2.8
8/09/79	C-2	380	1,700	250	1.5	10	2.9
8/11/79	C-2A	306.7	1,913	279	1.05	11	2.09
8/20/79	C-2B	334.2	-	-	1.99	16	2.07
8/27/79	C-2D	305.7	-	-	1.20	15	2.15
8/28/79	C-3D	303.8	2,017	376	1.34	16	2.22
8/29/79	C-2D	332.0	2,459	373	1.30	13	1.75
8/30/79	C-3D	324.6	2,108	317	1.31	12	1.77
8/31/79	C-2D	322.9	2,017	318	1.29	12	1.67
9/01/79	C-2D	310.3	1,900	316	1.65	15	1.88
9/05/79	C-2E	340.0	1,967	404	1.62	19	2.06
9/06/79	C-2E	344.0	1,967	308	1.48	15	1.86
9/07/79	C-2E	324.2	1,783	318	1.61	11	1.99
9/08/79	C-2E	299.8	1,909	258	1.44	13	1.64

(continued)

TABLE C-1 (continued)

Date	Test	Flue gas flow rate, ksft^3/min at 1 atm, 60°F	Inlet SO_2, ppm	Outlet SO_2, ppm	$CaCO_3$ stoichiometry	Venturi solids, %	Air stoichiometry, atoms O/mole SO_2
9/20/79	C-2F	328.3	-	-	1.22	7	1.87
9/21/79	C-2F	360.7	1,971	381	1.93	13	1.78
9/25/79	C-2G	325.5	1,988	380	1.08	9	1.74
10/02/79	C-2H	273.6	-	-	1.12	11	1.90
10/31/79	C-2T	307.5	1,607	-	1.07	4	1.64
11/01/79	C-2T	303.0	1,760	197	2.00	19	1.67
11/02/79	C-2T	303.0	1,679	185	2.19	30	1.82
11/14/79	D-1	286.8	-	-	1.40	4	1.76
11/15/79	D-1	303.1	-	-	2.12	19	1.96
11/18/79	D-2	293.2	-	-	1.44	4	1.69
11/19/79	D-2	298.4	-	-	1.88	14	1.61
12/05/79	D-4	340.0	1,583	273	1.13	9	2.05
12/06/79	D-4	339.3	1,442	144	-	-	1.85
12/07/79	D-4	345.7	1,746	282	1.06	9	-
12/08/79	D-4	332.6	1,725	257	1.18	13	1.80
12/09/79	D-4	326.3	1,858	268	1.13	7	1.70
12/10/79	D-4	328.3	1,750	280	1.26	9	1.65
12/11/79	D-4	321.9	1,717	222	1.32	10	1.89
12/12/79	D-4	322.6	1,742	202	1.48	10	1.72
12/13/79	D-4	352.5	1,742	245	1.08	7	1.50
12/14/79	D-4	355.3	1,892	248	1.85	22	1.65
12/18/79	D-5	-	-	-	1.14	8	-
12/19/79	D-5	338.9	1,844	214	1.58	17	2.12
12/20/79	D-5	337.0	1,579	164	1.39	8	2.26
12/21/79	D-5	296.2	1,325	160	1.01	3	2.79
1/04/80	D-6	299.9	1,800	181	1.32	17	-

TABLE C-2. BLEEDSTREAM LIQUID PHASE ANALYSIS

Date	Time	Test	Temp., °C	pH	Millimoles/liter SO_3^{2-}	SO_4^{2-}	Cl^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}	Relative saturation $CaSO_3 \cdot 1/2H_2O$	Relative saturation $CaSO_4 \cdot 2H_2O$	Residual electroneutrality, %	Solid phase oxidation, %	Comments
4/20/79	0830	B-1	46	5.7	1.8	21.9	40.1	2.0	23.2	12.5	1.4	1.2	-3.3	40	
4/22/79	0800	B-1	46	5.5	4.5	21.8	21.4	2.0	30.6	7.7	2.8	1.3	8.6	32	
4/23/79	0800	B-1	46	5.5	4.1	18.8	32.4	2.0	28.4	9.7	2.7	1.1	3.5	36	
4/30/79	0830	B-2	44	5.9	1.8	12.5	40.5	2.4	32.4	7.0	2.5	1.3	-2.2	62	
5/01/79	0745	B-2		5.8	5.8	17.4	36.8	2.4	25.8	11.1	1.1	0.97	2.8	63	
5/08/79	0800	B-2A	40	5.6	1.6	18.6	47.9	1.5	27.0	14.9	1.2	0.97	-0.33	67	Steady state
5/10/79	0800	B-2A	42	5.6	0.9	19.7	31.5	1.1	23.6	8.7	0.57	1.1	-4.1	99	Not steady state scrubber and oxidation up only 12 hrs prior to sampling
5/11/79	0800	B-2A	47	5.4	1.9	19.7	38.8	1.4	28.4	11.9	1.1	1.1	1.6	81	Steady state
5/14/79	0800	B-2A	47	5.5	3.4	16.3	38.9	2.2	28.7	12.8	2.2	0.91	7.1	72	Steady state
5/15/79	0830	B-2A	43	5.4	2.4	16.7	44.6	1.5	27.3	13.5	1.3	0.90	2.0	86	
5/16/79	0745	B-2A	44	5.8	2.1	21.0	42.2	1.3	28.4	12.8	2.2	1.1	-1.8	77	Steady state
5/24/79	0750	B-2	50	5.7	2.8	16.6	24.1	1.5	24.4	8.1	2.4	0.94	6.0	75	Steady state
5/25/79	0740	B-2	46	5.6	1.1	18.3	33.2	1.2	25.9	10.8	0.84	1.0	3.5	79	Steady state
5/26/79	0825	B-2	47	5.7	2.1	18.4	31.5	1.4	24.7	9.2	1.8	1.0	-1.4	79	Steady state
5/31/79	0800	B-2B	48	5.5	1.8	16.2	37.8	1.0	27.3	11.4	1.2	0.91	5.7	91	Oxidizing 23 hrs prior to sampling, vacuum filter down

(continued)

TABLE C-2 (continued)

Date	Time	Test	Temp., °C	pH	Millimoles/liter SO_3^{2-}	SO_4^{2-}	Cl^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}	Relative saturation $CaSO_3 \cdot 1/2H_2O$	Relative saturation $CaSO_4 \cdot 2H_2O$	Residual electroneutrality, %	Solid phase oxidation, %	Comments
6/01/79	0750	B-2	48	5.3	0.7	17.2	40.4	0.7	26.6	11.7	0.32	0.95	2.2	99+	Steady state
6/27/79	2150	C-1	51	5.8	0.1	16.7	31.5	NA	25.1	8.2	0.07	0.97	4.6	99+	Steady state
6/29/79	1145	C-1	50	5.7	0.02	17.4	27.3	NA	24.3	6.5	1.2	1.0	1.9	99+	Steady state
6/29/79	1400	C-1	50	6.4	0.05	16.9	32.0	NA	25.7	7.0	0.02	1.0	2.9	92	Venturi recirculation pump off. Overflow problems from absorber to venturi
8/09/79	0800		49	5.4	7.0	18.2	23.5	ND*	27.4	6.5	3.7	1.1	0.9	29.1	Baseline test
8/10/79	0800	C-2	49	5.0	2.5	18.6	37.9	ND	26.5	12.6	5.5	1.0	1.4	99.2	Startup
8/11/79	0800	C-2	50	5.8	9.9	14.7	29.5	2.8	27.3	9.0	1.0	0.8	1.6	98.8	Steady state
8/11/79	1630	C-2	51	5.3	12.3	16.1	36.7	ND	30.7	10.7	5.4	0.9	1.1	98.6	Steady state
8/15/79	1210	C-2	51	5.1	8.1	17.8	45.2	ND	29.4	13.2	2.3	1.0	-1.5	96.3	Not steady state
8/16/79	1315	SPV	50	5.4	17.5	9.2	37.6	ND	30.7	10.8	9.5	0.5	6.2	36.8	Baseline test
8/20/79	0725	C-2B	50	5.2	16.2	16.3	40.9	2.3	33.9	10.7	6.0	0.9	-0.7	95.9	Startup
8/20/79	1000	C-2B	48	5.5	5.0	16.7	40.9	2.5	28.6	11.2	3.3	0.9	0.3	98.1	Not steady state
8/26/79	1425	C-2C	47	5.3	13.0	16.2	46.4	2.3	32.2	0.9	5.9	0.9	-4.4	94.6	Steady state
8/27/79	0745	C-2C	48	5.2	1.9	17.1	45.0	2.5	26.5	11.5	0.7	0.9	-3.3	99.4	Steady state
8/28/79	1400	C-2D	51	5.2	11.1	13.7	52.4	ND	32.3	13.7	4.1	0.8	1.6	99.4	Steady state
8/29/79	0725	C-2D	49	5.2	15.7	15.9	39.8	1.9	31.2	10.1	5.6	0.9	-3.2	97.3	Steady state
8/30/79	0725	C-2D	48	5.1	7.5	16.3	35.4	2.1	29.5	9.3	2.5	1.0	-2.3	95.0	Steady state
8/31/79	0730	C-2D	48	5.3	8.9	16.4	30.8	2.4	27.8	8.1	3.9	0.9	0.3	98.0	Steady state
9/01/79	1020	C-2D	49	5.1	10.0	14.3	27.7	ND	26.2	7.8	2.8	0.8	2.9	93.8	Steady state
9/05/79	0800	C-2E	50	5.0	17.0	16.9	50.5	ND	35.9	13.7	4.7	0.9	-0.04	82.4	Steady state
9/06/79	0815	C-2E	49	5.3	10.4	16.9	32.4	2.7	26.2	12.6	3.7	0.9	0.9	91.4	Steady state
9/07/79	0750	C-2E	50	5.4	10.2	16.5	23.2	2.8	26.7	7.7	5.7	0.9	1.6	94.0	Steady state
9/08/79	0950	C-2E	47	5.4	9.0	16.3	28.2	2.3	27.2	8.8	4.7	0.9	1.9	92.5	Steady state
9/17/79	0745	SP	46	5.3	4.9	15.1	31.2	4.1	25.9	8.9	2.0	0.9	3.3	42.3	Startup
9/18/79	0730	SP	34	6.2	0.4	16.1	22.7	0.9	21.5	6.5	0.6	0.9	1.8	94.3	Steady state

(continued)

TABLE C-2 (continued)

Date	Time	Test	Temp., °C	pH	Millimoles/liter SO_3^{2-}	SO_4^{2-}	Cl^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}	Relative saturation $CaSO_3 \cdot 1/2H_2O$	Relative saturation $CaSO_4 \cdot 2H_2O$	Residual electroneutrality, %	Solid phase oxidation, %	Comments
9/20/79	0745	C-2F	44	5.4	0.1	17.7	22.3	2.9	19.5	8.1	0.1	0.9	-2.0	98.6	Steady state
9/21/79	0940	C-2F	48	5.3	4.6	17.1	36.8	2.9	26.4	10.4	1.9	0.9	-1.0	90.8	Steady state
9/25/79	0830	C-2G	46	5.3	9.9	26.4	25.4	2.1	25.9	8.1	3.7	1.3	-18.0	92.6	Steady state
9/25/79	1600	C-2G	46	5.5	0.2	20.3	20.6	2.6	19.6	8.8	0.1	1.0	-4.2	95.5	Steady state
10/02/79	0930	C-2H	40	4.9	ND**	22.3	13.8	2.4	17.8	11.0	0.0	1.0	0.6	97.2	Steady state
10/02/79	1330	C-2H	44	5.2	ND	21.0	15.0	2.5	17.6	9.8	0.0	0.9	-1.1	95.3	Steady state
10/10/79	0800	C-2I	50	5.8	5.6	17.2	34.9	3.1	26.1	7.2	5.9	1.0	-7.7	69.7	Steady state, low oxidation due to broken agitator impeller
10/14/79	0740	C-2M	39	5.7	12.7	17.2	12.3	4.3	25.4	5.1	10.9	1.0	-2.0	75.2	
10/15/79	0740	C-2M	38	5.3	13.0	18.2	16.3	2.3	25.7	7.7	5.3	1.0	0.7	76.9	
10/16/79	0740	C-2M	44	5.4	21.6	16.0	12.7	4.0	28.4	6.4	10.9	0.9	0.6	86.5	
10/17/79	-	C-2M	37	5.6	11.4	16.7	22.4	5.5	26.2	7.5	8.4	0.9	-2.5	57.3	
10/22/79	0810	C-2N	40	5.4	6.7	20.1	19.4	2.5	20.7	12.1	2.8	0.9	-0.2	87.8	Not steady state
10/25/79	0800	C-2O	42	7.6	1.1	18.5	33.0	2.0	24.7	10.7	3.4	1.0	-1.1	85.6	Steady state
10/28/79	0845	C-2Q	39	5.7	10.8	17.2	16.3	3.2	26.4	4.2	9.7	1.0	-3.6	93.0	Not steady state
10/28/79	1735	C-2Q	44	5.6	4.7	17.6	28.8	2.3	25.9	7.8	3.6	1.0	-1.5	98.7	Not steady state
10/31/79	0800	C-2T	42	5.4	5.2	15.8	32.2	2.1	25.0	8.6	2.7	0.9	-1.4	99.4	Steady state
11/01/79	0815	C-2T	48	5.4	7.7	17.4	46.8	2.0	28.2	13.2	3.9	0.9	-4.1	99.6	Steady state
11/02/79	0810	C-2T	47	5.1	9.9	18.0	31.2	2.2	27.2	10.1	3.0	1.0	-2.0	99.6	Steady state
11/13/79	0800	D-1	36	5.1	0.1	15.4	21.4	1.7	20.3	5.6	0.0	0.9	-0.1	99.0	Steady state
11/14/79	0800	D-1	42	5.0	9.8	16.6	27.4	2.1	26.7	9.0	2.3	0.9	0.9	99.3	Steady state
11/15/79	0815	D-1	42	5.1	11.2	17.2	26.9	1.9	27.2	9.0	3.5	1.0	-0.01	99.3	Steady state
11/18/79	0920	D-2	41	5.3	8.8	19.4	10.6	2.3	24.1	5.5	3.6	1.1	0.3	98.4	Steady state
11/19/79	0800	D-2	44	6.3	7.3	16.8	28.0	3.0	26.2	7.5	1.4	0.9	-6.5	99.3	Steady state
11/27/79	0905	D-3	44	5.6	0.2	15.2	24.2	2.6	21.0	3.0	0.2	0.9	-7.8	98.1	Steady state
11/28/79	0800	D-3	44	5.7	1.9	17.4	18.7	3.0	27.4	11.0	1.7	1.0	+22.0	97.3	Steady state
12/05/79	0800	D-4	43	6.0	ND	17.9	21.0	3.2	22.4	5.6	0.0	1.0	-1.0	97.5	Not steady state
12/06/79	1250	D-4	43	5.9	0.1	16.2	24.8	1.9	22.8	5.6	0.1	1.0	0.4	NA	Steady state
12/08/79	0750	D-4	39	5.8	ND	17.7	15.8	1.7	18.7	6.0	0.0	0.9	-1.1	98.9	Steady state
12/09/79	1005	D-4	43	5.5	ND	17.5	20.9	2.9	20.5	6.0	0.0	1.0	-2.4	96.6	Steady state
12/10/79	0845	D-4	43	5.6	0.2	17.9	20.0	2.7	25.0	7.8	1.4	1.1	+11.0	95.4	Steady state

(continued)

TABLE C-2 (continued)

					Millimoles/liter										
Date	Time	Test	Temp., °C	pH	SO_3^{2-}	SO_4^{2-}	Cl^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}	Relative saturation $CaSO_3 \cdot 1/2H_2O$	Relative saturation $CaSO_4 \cdot 2H_2O$	Residual electroneutrality, %	Solid phase oxidation, %	Comments
12/11/79	-	D-4	41	5.8	0.4	18.2	10.7	3.2	17.6	4.8	0.3	1.0	-4.0	97.5	Steady state
12/12/79	-	D-4	45	5.5	4.6	18.3	12.0	3.1	22.5	4.3	2.7	1.1	2.1	99.4	Steady state
12/13/79	0810	D-4	41	5.4	0.6	18.2	14.3	2.5	17.6	7.4	0.3	0.9	-2.8	97.8	Steady state
12/14/79	0810	D-4	42	5.3	5.8	18.3	17.2	2.9	22.8	6.6	2.3	1.0	-0.3	97.6	Steady state
12/18/79	0820	D-5	37	5.2	ND	18.3	17.4	3.2	18.9	8.2	0.0	0.9	1.8	99.2	Not steady state
12/19/79	0745	D-5	41	5.8	1.9	20.4	28.6	3.9	24.8	8.6	1.9	1.1	-4.7	96.6	Steady state
12/20/79	0745	D-5	41	5.7	0.2	13.3	28.8	2.4	19.2	6.7	0.2	0.7	-3.6	98.9	Steady state
12/21/79	0810	D-5	36	5.4	0.1	16.0	34.3	2.1	24.1	8.5	0.0	0.9	-0.07	99.7	Steady state
1/04/80	1050	D-6	41	5.6	9.9	18.1	19.9	3.1	22.1	8.9	6.4	0.9	-6.0	99.4	Steady state

ND - No data.

NA - Not analyzed.

ND* - Where CO_3^{2-} values are missing, an average of 2.76 MM is used in determining REN.

ND** - Where SO_3^{2-} values are marked ND, the concentration is near the detection limit for the iodine/thiosulfate method. A value of 0.0 is used in determining REN.

TABLE C-3. SPECIAL TESTING LIQUID PHASE ANALYSIS

Date	Sample location	Test	Temp., °C	pH	Millimoles/liter SO_3^{2-}	SO_4^{2-}	Cl^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}	Relative saturation $CaSO_3 \cdot 1/2H_2O$	Relative saturation $CaSO_4 \cdot 2H_2O$	Residual electroneutrality, %	Solid phase oxidation, %	Comments
4/14/79	Venturi tank	Baseline sampling	39	5.7	4.0	31.2	19.7	NA	36.1	6.6	4.1	2.0	-0.2	29.6	Oxidation system not in service
4/17/79	Venturi tank	Baseline sampling	31	5.5	12.6	20.1	27.8	NA	29.7	8.6	8.1	1.2	-3.3	67.0	Thickener not in service
5/02/79	Venturi tank	Baseline sampling	45	5.4	4.5	16.7	27.8	1.8	24.8	9.2	2.3	0.9	4.3	54.8	Oxidizing air on, not following load
5/02/79	Venturi tank	Baseline sampling	41	4.8	27.8	23.5	35.0	3.2	45.2	10.7	5.0	1.5	2.2	NA	
5/02/79	Absorber tank	Baseline sampling	52	5.5	13.2	17.9	28.9	6.5	28.3	12.0	7.8	0.9	1.9	NA	
5/02/79	Absorber bottoms	Baseline sampling	50	5.2	19.0	21.0	29.8	3.7	32.5	12.1	6.4	1.1	-0.5	NA	
5/07/79	Thickener feed	Baseline sampling	48	5.7	2.6	17.7	38.3	2.4	26.2	12.8	2.1	0.9	3.0	56.8	Oxidizing air on, not following load
5/07/79	Absorber feed	Baseline sampling	53	5.6	8.7	17.1	36.8	6.8	27.7	14.8	5.3	0.9	4.7	58.2	
5/07/79	Absorber bottoms	Baseline sampling	51	5.0	12.9	17.2	35.6	3.0	28.4	13.0	2.8	0.9	1.5	NA	
5/18/79	Absorber bottoms	Baseline sampling	48	5.0	13.4	18.0	42.8	2.5	34.7	14.7	3.3	1.0	5.0	56.7	No test while waiting for new air flow transmitter
5/18/79	Absorber recycle	Baseline sampling	51	5.4	8.3	18.8	44.8	4.8	30.6	9.6	4.0	1.1	-7.6	45	
5/18/79	Venturi bottoms	Baseline sampling	49	4.5	20.9	24.0	53.7	2.2	44.3	16.3	2.0	1.4	0.0	59.7	

(continued)

TABLE C-3 (continued)

Date	Sample location	Test	Temp., °C	pH	Millimoles/liter						Relative saturation $CaSO_3 \cdot 1/2H_2O$	Relative saturation $CaSO_4 \cdot 2H_2O$	Residual electroneutrality, %	Solid phase oxidation, %	Comments
					SO_3^{2-}	SO_4^{2-}	Cl^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}					
5/18/79	Thickener feed	Baseline sampling	51	5.5	8.5	17.7	53.3	3.1	33.4	15.7	5.4	1.0	0.5	52.5	No test while waiting for air flow transmitter
5/21/79	Thickener feed	Baseline sampling (0920)	49	5.2	8.2	18.5	66.8	2.2	36.5	2.0	3.2	1.0	-3.1	39.2	
5/21/79	Thickener feed	Baseline sampling (0947)	51	5.1	8.5	18.5	63.4	NA	37.1	16.9	2.8	1.0	0.0	38.7	
5/21/79	Thickener feed	Baseline sampling (0918)	51	5.0	8.6	18.9	68.6	NA	37	16.9	2.1	1.0	-3.3	38.2	
6/11/79	Absorber recycle	Baseline sampling	48	5.1	14.1	20.7	37.0	36.8	33.9	11.4	4.6	1.2	-2.7	66.7	Flue gas flow through D-train too high
6/11/79	Absorber bottoms	Baseline sampling	45	5.2	15.7	22.9	34.3	41.1	35.2	11.8	5.7	1.3	-3.5	73.9	
6/11/79	Venturi feed	Baseline sampling	46	5.7	8.1	19.9	44.3	28.6	35.1	12.7	7.7	1.1	-2.8	80.7	
6/11/79	Venturi feed	Baseline sampling	45	5.6	16.6	24.5	50.9	43.4	42.1	13.4	13.7	1.3	-9.8	87.8	
6/18/79	Absorber bottom	Baseline sampling	48	5.9	3.6	18.2	23.0	NA	27.5	8.5	4.6	1.1	9.4	24.6	No oxidizing air flow, out of diesel fuel
6/18/79	Venturi bottom	Baseline sampling	46	5.7	5.0	15.5	27	NA	28.7	8.9	4.8	0.9	12.2	24.9	

NA - Not analyzed

TABLE C-4. ABSORBER BOTTOMS LIQUID PHASE ANALYSIS

Date	Time	Test	Temp., °C	pH	Millimoles/liter SO_3^{2-}	SO_4^{2-}	Cl^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}	Relative saturation $CaSO_3 \cdot 1/2H_2O$	Relative saturation $CaSO_4 \cdot 2H_2O$	Residual electroneutrality, %	Solid phase oxidation, %	Comments
8/16/79	1315	SPB	51	5.2	1.9	22.2	28.2	-	26.3	6.4	6.5	1.3	6.5	33.8	Baseline test
9/05/79	0800	C-2E	53	4.8	10.6	22.4	42.6	-	33.9	13.5	1.8	1.2	1.8	83.8	Steady state
10/02/79	1330	C-2H	47	4.5	6.0	21.5	11.3	3.3	19.8	9.8	0.3	1.0	-0.3	90.9	Steady state
10/10/79	0800	C-2I	53	5.4	7.6	16.9	25.7	2.1	23.6	8.0	3.6	0.9	-4.0	79.2	Steady state, low oxidation due to broken agitator impeller
10/14/79	0740	C-2M	40	5.6	11.3	17.8	12.0	3.3	29.9	5.8	9.2	1.1	11.0	77.5	
10/15/79	0740	C-2M	42	5.3	11.7	21.2	12.4	2.3	28.2	7.2	5.0	1.2	3.9	76.7	
10/16/79	0740	C-2M	44	5.4	15.7	22.1	10.1	3.2	29.7	6.6	8.1	1.3	0.8	86.2	
10/17/79	-	C-2M	44	5.5	9.7	23.4	16.2	2.9	29.4	7.3	6.1	1.3	-0.8	67.1	
10/22/79	0810	C-2M	42	4.7	5.9	21.5	17.1	3.2	20.9	12.0	0.6	1.0	1.0	89.8	Not steady state
10/25/79	0800	C-2O	40	7.0	8.4	21.2	25.8	4.8	27.9	9.9	33.0	1.1	-1.0	93.7	Steady state
10/28/79	0845	C-2Q	44	5.4	9.7	31.1	17.3	4.4	36.9	5.7	5.6	1.9	-4.5	95.7	Not steady state
10/28/79	-	C-2Q	42	5.2	9.7	28.3	17.3	4.4	34.2	5.7	-	-	-4.0	-	Not steady state
10/28/79	1735	C-2Q	42	5.6	5.1	20.2	22.6	2.1	26.7	7.6	3.9	1.2	-0.1	98.7	Not steady state
10/31/79	0800	C-2T	42	-	3.5	18.3	33.9	1.9	25.4	10.4	1.2	1.0	-1.2	99.4	Steady state
11/01/79	0815	C-2T	45	5.2	3.7	20.5	35.9	2.3	26.7	12.2	1.3	1.1	-1.1	99.4	Steady state
11/02/79	0810	C-2T	42	5.2	4.3	20.6	23.7	2.5	25.9	9.5	1.5	1.1	2.2	99.7	Steady state
11/13/79	0800	D-1	41	4.8	3.5	17.5	29.9	2.7	25.2	9.3	0.5	1.0	0.9	98.9	Steady state
11/14/79	0800	D-1	42	4.9	4.1	21.0	24.9	2.7	25.7	9.0	0.8	1.2	-0.9	99.2	Steady state
11/15/79	0815	D-1	43	5.1	7.7	19.9	22.5	2.4	26.9	9.0	2.4	1.1	1.6	99.1	Steady state
11/19/79	0800	D-2	43	5.4	4.8	19.5	25.4	4.2	26.4	8.4	2.5	1.1	-0.04	99.4	Steady state
11/27/79	0905	D-3	38	5.3	5.6	18.8	21.7	3.0	26.1	5.7	2.7	1.1	-1.7	97.8	Steady state
11/28/79	0800	D-3	43	5.3	8.8	21.2	12.8	3.4	27.7	9.4	3.5	1.2	11.0	98.2	Steady state
12/05/79	0900	D-4	43	5.2	4.1	19.6	16.1	2.5	23.5	5.6	1.4	1.1	-1.0	96.9	Not steady state
12/06/79	1225	D-4	46	5.6	4.8	18.1	17.3	1.7	24.0	4.6	3.6	1.1	-1.8	98.4	Steady state
12/07/79	0745	D-4	43	5.6	4.5	17.6	11.3	1.8	21.1	5.5	3.1	1.0	3.0	98.9	Steady state

(continued)

TABLE C-4 (continued)

Date	Time	Test	Temp., °C	pH	Millimoles/liter						Relative saturation $CaSO_3 \cdot 1/2H_2O$	Relative saturation $CaSO_4 \cdot 2H_2O$	Residual electroneutrality, %	Solid phase oxidation, %	Comments
					SO_3^{2-}	SO_4^{2-}	Cl^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}					
12/08/79	0750	D-4	43	5.0	4.8	20.8	10.4	1.5	22.7	5.9	1.0	1.2	1.6	97.0	Steady state
12/10/79	0845	D-4	41	5.5	5.2	19.2	11.4	2.7	23.9	4.5	3.2	1.1	1.7	94.8	Steady state
12/11/9	-	D-4	42	5.4	5.3	21.2	9.2	2.4	21.2	4.9	2.4	1.1	-6.3	97.5	Steady state
12/12/79	-	D-4	45	5.4	8.1	21.0	8.0	2.7	25.5	3.6	4.1	1.3	-0.8	99.9	Steady state
12/13/79	0810	D-4	48	5.2	4.6	20.8	13.0	2.6	21.8	7.6	1.4	1.1	-0.6	99.4	Steady state
12/14/79	0810	D-4	42	5.4	7.4	20.8	12.2	3.1	25.6	6.7	3.8	1.2	3.5	99.1	Steady state
12/18/79	0820	D-5	40	5.4	5.3	21.2	12.2	3.7	22.2	6.9	2.4	1.1	-1.8	98.4	Not steady state
12/19/79	0745	D-5	43	5.5	6.8	21.7	21.3	3.3	25.9	7.9	4.1	1.2	-4.4	96.5	Steady state
12/20/79	0745	D-5	36	5.5	6.4	18.8	28.5	3.6	27.4	8.1	4.1	1.1	-1.9	83.0	Steady state
12/21/79	0810	D-5	42	5.4	3.0	17.5	23.5	1.4	22.6	7.0	1.5	1.0	-1.7	97.4	Steady state
1/04/80	1050	D-6	41	5.5	5.8	21.8	14.0	4.5	22.5	8.0	3.2	1.1	-3.3	98.6	Steady state

TABLE C-5. SOLID PHASE ANALYSES OF THICKENER FEED

			Solid phase analysis, mg/g solid												
Date	Test	pH	Ca^{2+}	SO_3^{2-}	SO_4^{2-}	CO_3^{2-}	Mg^{2+}	Acid insoluble	Ca/SO_x ratio, lb-m/lb-m	$CaCO_3$ added, lb-m/min	SO_2 absorbed, lb-m/min	Oxygen added, lb-atoms/min	O/SO_2 ratio, lb-at/lb-m	Oxidation, %	Filter cake, % solids
4/20/79	B-1	5.7	176	158	112	ND	5.5	385	1.4	ND	ND	ND	ND	40	62
4/22/79	B-1	5.4	198	224	126	ND	4.2	293	1.2	2.2	1.8	0.8	0.4	32	71
4/23/79	B-1	5.5	184	172	114	ND	5.7	290	1.6	2.0	1.2	0.8	0.7	36	66
4/30/79	B-2	5.9	185	110	211	52	4.2	310	1.3	ND	ND	ND	0.7	62	62
5/01/79	B-2	5.8	177	109	222	42	3.5	344	1.2	1.9	1.6	1.3	0.8	63	68
5/08/79	B-2	5.6	174	98	240	42	3.4	342	1.2	2.0	1.7	2.5	1.5	67	71
5/10/79	B-2	5.6	158	4	317	51	2.9	353	1.2	1.1	0.9	2.5	2.8	99	74
5/11/79	B-2	5.7	146	51	257	45	2.6	374	1.1	1.9	1.7	2.5	1.5	81	79
5/14/79	B-2	5.5	178	75	231	53	2.8	344	1.3	1.5	1.2	2.5	2.1	72	75
5/15/79	B-2	5.4	188	41	287	98	3.4	284	1.3	2.0	1.5	2.5	1.7	86	77
5/16/79	B-2	5.8	174	64	259	65	2.8	339	1.2	2.1	1.8	2.5	1.4	77	80
5/24/79	B-2	5.7	183	79	279	51	3.0	272	1.2	2.2	1.8	3.0	1.7	75	V.F. down
5/25/79	B-2	5.6	196	67	310	48	2.8	247	1.2	2.0	1.7	2.9	1.7	80	82
5/26/79	B-2	5.7	207	78	347	50	2.7	272	1.1	1.6	1.5	3.2	2.1	79	70
5/31/79	B-2	5.5	181	28	348	ND	1.6	270	1.2	1.4	1.2	2.9	2.4	91	V.F. down
6/01/79	B-2	5.3	166	1	354	ND	1.1	315	1.1	1.5	1.4	2.8	2.0	99+	V.F. down
8/09/79	-	5.4	180	185	91	-	2	376	1.4	-	-	-	-	29	-
8/10/79	STU	5.0	143	2	336	12	0	367	1.0	-	-	-	-	99	-
8/11/79	C-2	5.8	146	3	326	38	2	348	1.1	2.3	1.3	2.8	2.1	99	81.8
8/11/79	C-2	5.3	196	4	336	100	2	235	1.4	2.3	1.3	2.8	2.1	99	75.6
8/15/79	C-2	5.1	155	10	326	49	2	337	1.1	-	-	-	-	96	-
8/16/79	SPV	5.4	216	190	133	140	3	277	1.5	-	-	-	-	37	-
8/20/79	C-2B	5.2	232	10	267	197	4	187	2.0	-	1.5	3.2	2.1	96	-
8/20/79	C-2B	5.5	220	5	297	179	3	194	1.8	-	1.5	3.2	2.1	98	-
8/26/79	C-2C	5.3	153	13	270	78	2	253	1.3	-	-	-	-	95	-
8/27/79	C-2C	5.2	167	2	332	59	2	275	1.2	-	1.6	3.4	2.1	99	-
8/28/79	C-2D	5.2	181	2	323	65	2	257	1.4	2.9	1.3	2.9	2.2	99	-
8/28/79	C-2D	5.2	176	7	315	82	2	246	1.3	2.9	1.3	2.9	2.2	97	-

(continued)

TABLE C-5 (continued)

Date	Test	pH	Solid phase analysis, mg/g solid Ca^{2+}	SO_3^{2-}	SO_4^{2-}	CO_3^{2-}	Mg^{2+}	Acid insol-uble	Ca/SOx ratio, lb-m/lb-m	CaCO3 added, lb-m/min	SO2 absorbed, lb-m/min	Oxygen added, lb-atoms/min	O/SO2 ratio, lb-at/lb-m	Oxidation, %	Filter cake, % solids
8/30/79	C-2D	5.1	190	14	330	67	1	225	1.3	2.9	1.5	2.7	1.8	95	-
8/31/79	C-2D	5.3	182	6	332	115	2	247	1.3	3.1	1.4	2.4	1.7	98	-
9/01/79	C-2D	5.1	220	17	305	108	2	242	1.7	2.3	1.3	2.4	1.9	94	-
9/05/79	C-2E	5.0	204	46	256	121	4	263	1.6	3.1	1.4	2.9	2.1	82	-
9/06/79	C-2E	5.3	194	22	286	112	4	258	1.5	3.6	1.5	2.8	1.9	91	-
9/07/79	C-2E	5.4	217	16	304	132	3	209	1.7	3.1	1.3	2.5	2.0	94	-
9/08/79	C-2E	5.4	185	19	284	87	2	261	1.5	2.4	1.3	2.1	1.6	92	77.3
9/17/79	SP	5.3	233	198	174	95	3	376	1.4	-	-	-	-	42	-
9/18/79	SP	6.2	209	17	335	106	3	252	1.4	-	-	-	-	94	-
9/20/79	C-2F	5.4	216	5	418	61	3	300	1.2	-	1.2	2.2	1.9	99	-
9/21/79	C-2F	5.3	216	24	233	173	2	248	2.0	3.2	1.5	2.7	1.8	89	86.1
9/21/79	C-2F	5.3	211	20	237	173	4	243	2.0	3.2	1.5	2.7	1.8	91	86.1
9/25/79	C-2G	5.3	211	22	326	101	4	392	1.5	2.4	1.4	2.4	1.7	93	64.9
9/25/79	C-2G	5.5	157	13	326	26	2	336	1.1	2.4	1.4	2.4	1.7	95	86.1
10/02/79	C-2H	4.9	166	9	362	26	1	282	1.1	-	1.3	2.4	1.9	97	-
10/02/79	C-2H	5.2	160	14	328	46	1	306	1.1	-	1.3	2.4	1.9	95	-
10/10/79	C-2I	5.8	200	66	182	159	4	308	1.9	-	-	-	-	70	-
10/14/79	C-2M	5.7	236	50	181	204	5	210	2.4	-	-	-	-	75	73.5
10/15/79	C-2M	5.3	240	44	176	204	5	209	2.6	-	-	-	-	77	-
10/16/79	C-2M	5.4	221	26	203	219	5	238	2.3	-	-	-	-	86	86.3
10/17/79	C-2M	5.6	190	126	204	85	4	290	1.3	-	-	-	-	57	-
10/22/79	C-2N	5.4	164	32	277	64	3	334	1.3	-	-	-	-	88	-
10/25/79	C-2O	7.6	103	22	160	60	4	586	1.4	-	-	-	-	86	-
10/28/79	C-2Q	5.7	169	13	203	147	4	381	1.9	-	-	-	-	93	84.0
10/28/79	C-2Q	5.6	209	3	290	136	4	249	1.8	-	-	-	-	99	85.0
10/31/79	C-2T	5.4	153	2	342	-	2	340	1.1	2.4	1.3	2.1	1.6	99	-
11/01/79	C-2T	5.4	220	1	262	-	5	210	2.1	3.2	1.2	2.1	1.7	100	-

(continued)

TABLE C-5 (continued)

			Solid phase analysis, mg/g solid						Ca/SOx ratio, lb-m/lb-m	CaCO3 added, lb-m/min	SO2 absorbed, lb-m/min	Oxygen added, lb-atoms/min	O/SO2 ratio, lb-at/lb-m	Oxidation, %	Filter cake, % solids
Date	Test	pH	Ca^{2+}	SO_3^{2-}	SO_4^{2-}	CO_3^{2-}	Mg^{2+}	Acid insoluble							
11/02/79	C-2T	5.1	231	1	252	-	5	199	2.3	3.0	1.2	2.2	1.8	100	-
11/13/79	D-1	5.1	170	3	375	-	2	276	1.1	-	-	-	-	99	-
11/14/79	D-1	5.0	168	2	285	-	5	336	1.5	-	1.2	2.1	1.8	99	-
11/15/79	D-1	5.1	235	2	264	-	4	189	2.2	-	1.1	2.1	2.0	99	87.3
11/18/79	D-2	5.3	182	4	298	-	3	304	1.5	-	1.5	2.6	1.7	98	85.1
11/19/79	D-2	6.3	215	2	272	182	3	215	1.9	-	1.3	2.2	1.6	99	85.7
11/27/79	D-3	5.6	148	5	290	56	2	365	1.2	-	-	-	-	98	-
11/28/79	D-3	5.7	178	7	308	109	3	314	1.4	-	-	-	-	97	-
12/05/79	D-4	6.0	160	7	331	43	2	352	1.1	1.7	1.2	2.4	2.1	97	-
12/07/79	D-4	-	142	8	310	33	2	379	1.1	1.7	1.3	-	-	97	89.0
12/08/79	D-4	5.8	165	3	332	59	2	334	1.2	1.8	1.3	2.3	1.8	99	90.0
12/09/79	D-4	5.5	147	9	303	26	2	413	1.2	2.2	1.4	2.3	1.7	97	-
12/10/79	D-4	5.6	177	13	321	75	2	208	1.3	2.0	1.3	2.1	1.7	95	-
12/11/79	D-4	5.8	190	7	336	90	2	240	1.3	1.9	1.3	2.4	1.9	97	89.0
12/12/79	D-4	5.5	194	2	313	134	3	239	1.5	1.8	1.3	2.3	1.7	99	88.7
12/13/79	D-4	5.4	141	6	305	-	2	377	1.1	1.8	1.4	2.1	1.5	98	-
12/14/79	D-4	5.3	215	6	271	160	3	187	1.9	2.2	1.5	2.5	1.6	98	-
12/18/79	D-5	5.2	168	2	351	40	0	283	1.1	-	-	-	-	99	85.0
12/19/79	D-5	5.8	202	9	296	166	3	176	1.6	2.4	1.5	3.1	2.1	97	87.3
12/20/79	D-5	5.7	177	3	303	91	3	279	1.4	2.2	1.3	2.8	2.3	99	86.8
12/21/79	D-5	5.4	135	1	319	31	2	374	1.0	1.5	0.9	2.5	2.8	100	-
1/04/80	D-6	5.6	191	2	345	100	2	-	1.3	2.3	1.3	-	-	99	90.1

ND - No data

TABLE C-6. SOLID PHASE ANALYSES OF THICKENER UNDERFLOW

		Solid phase analysis, mg/g solid							Oxidation,
Date	Test	Ca^{2+}	SO_3^{2-}	SO_4^{2-}	CO_3^{2-}	Mg^{2+}	Ash	pH	%
4/20/79	B-1	192	125	138	ND	6.4	365	6.1	48
4/22/79	B-1	221	138	53	ND	7.4	255	6.2	24
4/23/79	B-1	213	108	80	ND	8.4	285	5.9	38
4/30/79	B-2	196	89	182	123	5.2	297	6.3	63
5/01/79	B-2	185	66	228	93	4.6	320	6.3	74
5/08/79	B-2	180	70	256	65	4.0	321	5.9	75
5/10/79	B-2	165	0	290	86	3.5	325	5.6	99+
5/11/79	B-2	176	54	234	87	3.5	355	5.9	78
5/14/79	B-2	199	63	194	117	3.5	313	5.6	72
5/15/79	B-2	179	60	294	27	3.1	321	6.0	81
5/16/79	B-2	174	58	231	73	2.6	350	6.0	77
5/24/79	B-2	192	70	280	51	3.3	254	5.9	77
5/25/79	B-2	201	56	308	70	3.1	228	6.1	82
5/26/79	B-2	217	56	350	91	3.2	263	6.4	84
5/31/79	B-2	194	32	341	ND	1.8	245	6.5	90
6/01/79	B-2	171	0.8	373	ND	1.1	283	6.0	99+
6/27/79	C-1	180	0	296	306	1.5	366	6.4	99+
6/29/79	C-1	193	23	270	82	1.6	342	6.1	91

ND - No data

TABLE C-7. SETTLING RATE DATA

Date	Time	Test	Point of compression Time, min	 Distance, ml	Settling rate, ft/hr	Final pulp vol., ml	Slurry solids, %	Oxidation, %	Slurry temp., °C
4/20/79	0830	B-1	70	542	0.51	338	12.7	40	46
4/22/79	0800	B-1	40	599	0.98	275	5.3	32	46
4/23/79	0800	B-1	40	560	0.91	290	9.0	36	46
4/30/79	0830	B-2	40	540	0.88	320	11.7	61	44
5/01/79	0765	B-2	30	659	1.44	240	8.6	63	38
5/08/79	0800	B-2A	36	621	1.13	245	9.5	67	40
5/11/79	0800	B-2A	22	695	2.07	198	11.2	81	47
5/14/79	0800	B-2A	24	622	1.7	232	12.9	72	47
5/15/79	0830	B-2A	19	551	1.9	253	18.5	85	43
5/16/79	0745	B-2A	22	645	1.9	210	14.7	77	44
5/24/79	0750	B-2	14	725	3.4	177	8.0	74	50
5/25/79	0740	B-2	16	710	2.9	180	8.3	79	46
5/26/79	0825	B-2	24	640	1.8	221	11.3	79	47
5/31/79	0800	B-2B	15	780	3.4	156	11	91	48
6/01/79	0750	B-2	10	830	5.5	140	8.9	99	48
6/14/79	0750	B-25	12	825	4.5	140	10.8	97	43
6/27/79	2150	C-1	9.5	825	5.7	140	9.3	99+	51
6/29/79	1145	C-1	8.5	875	6.8	115	9.8	99+	50
6/29/79	1400	C-1	15	830	3.7	140	10.2	92	50

Each 100 ml settled = 1-5/16 cm distance for graduated cylinder used.

TABLE C-8. COMPILED FILTER LEAF DATA

Date	Test	Sample location	Solids wt. %	Oxidation, %	pH	Filtrate volume, ml	Filtrate quality	Wet filter cake wt. g	Dry filter cake wt. g	Filter cake solids, wt %	Filter cake thickness, in.	Filter cake ease of separation[a]
4/20/79	B-1	Feed	12.7	37	5.7		Fair to good	187.31	101.61	54	3/4	Good
		Underflow	31.3	48	6.0		Fair	499.51	307.09	61	1-3/4	Good
4/22/79	B-1	Feed	5.3	32	5.5		Good	136.33	67.02	49	1/4	O.K.
		Underflow	20.4	24	6.0		Good	295.82	182.40	61	1-3/4	O.K.
4/23/79	B-1	Feed	9.0	35	5.5	820	Fair	149.17	81.36	54	3/8	O.K.
		Underflow	19.3	38	6.1	1,250	Fair	325.87	205.63	63	3/4	Good
4/30/79	B-2	Feed		62	5.9	725	Good	158.98	97.61	61	3/8	Good
		Underflow		63	6.6	875	Good	330.88	229.62	70	7/8	Good
5/01/79	B-2	Feed	8.6	62	5.8	800	Good	121.56	72.71	60	3/8	Good
		Underflow	32.3	74	6.3	805	Good	415.20	288.79	70	1-1/8	Good
5/08/79	B-2	Feed	9.6	67	5.6	750	Fair	154.74	87.24	56	3/8	Good
		Underflow	20.7	75	5.9	1,000	Fair	144.96	77.96	51	3/4	Good
5/10/79	B-2	Feed	8.9	98	5.6	1,525	Good	217.98	99.94	46	3/4	Good
		Underflow	17.8	99+	5.6	2,325	Good	543.34	397.94	73	1-5/8	Good
5/11/79	B-2	Feed	11.2	81	5.4	875	Good	116.63	73.70	63	1/4	Good
		Underflow	35.7	78	6.0	1,025	Good	331.16	241.10	73	7/8	Good
5/14/79	B-2	Feed	12.9	72	5.5	840	Good	129.85	76.54	59	5/16	Good
		Underflow	1.9	72	5.6	3,150	Good	41.60	26.69	64	1/8	Good
5/15/79	B-2	Feed	18.5	86	5.4	760	Good	139.24	82.74	60	3/8	Good
		Underflow	26.8	80	6.0		Good	823.84	561.64	69	2-3/8	Good
5/16/79	B-2	Feed	14.7	77	5.8	860	Good	133.90	81.52	60	5/16	Good
		Underflow	28.9	77	6.0	828	Good	823.84	561.64	69	2-3/8	Good
5/25/79	B-2	Feed	8.2	75	5.7	910	Good	93.20	51.50	55	3/16	Good
		Underflow	22.0	77	9.2		Good	233.61	165.70	70	5/8	Good
5/26/79	B-2	Feed	11.3	79	5.7	720	Fair	90.97	51.60	57	1/4	Good
		Underflow	31.7	84	6.5	1,200	Fair	307.65	217.22	71	1	Good
5/31/79	B-2	Feed	10.5	91	5.5	1,050	Good	90.73	57.33	63	1/4	Good
		Underflow	25.9	90	6.5	750	Good	151.28	111.60	74	1/2	Good
6/01/79	B-2	Feed	8.9	99+	5.3	990	Fair	55.67	43.37	78	1/4	Good
		Underflow	17.8	99+	6.0	800	Fair	134.00	109.00	82	3/8	Good
6/27/79	C-1	Feed	9.0	99	5.7	900	Poor	44.27	33.04	74	1/8	Fair
		Underflow	14.4	100	6.3	790	Good	91.95	69.62	76	5/8	Fair
6/29/79	C-1	Feed	9.8	99+	5.6	930	Fair	36.76	28.35	85	1/8	Fair
		Underflow	31.6	99+	6.4	1,060	Fair	334.75	283.53	85	1-1/8	Fair
6/29/79	C-1	Feed	10.2	92	6.4	1,075	Fair	63.04	40.35	64	3/16	Fair
		Underflow	35.3	92	6.8	485	Fair	253.04	192.45	76	9/16	Fair

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a. Based on observation: good indicates relatively easy separation, fair indicates minor sticking or some difficulty of separation.

TABLE C-9. COMPARISON OF PLANT VACUUM FILTER DATA AND FILTER LEAF TEST DATA

		Vacuum filter data		Filter leaf test data	
Date	Test	Solids, %	Average cake thickness, in.	Solids, %	Cake thickness, in.
4/20/79	B-1	61.2	3/4	61.5	1-3/4
4/22/79	B-1	70	7/16	61.7	3/4
4/23/79	B-1	65	3/8	63.1	3/4
4/30/79	B-2	68.1	3/4	69.6	7/8
5/01/79	B-2	67.6	7/8	69.6	1-1/8
5/08/79	B-2	71.3	3/4	51.0	3/4
5/10/79	B-2	73.8	3/4	73.2	1-5/8
5/11/79	B-2	78.5	7/8	72.8	7/8
5/14/79	B-2	75.4	3/8 (avg)	64.2	1/8
5/15/79	B-2	76.5	5/8 (avg)	68.2	2-3/8
5/16/79	B-2	79.5	5/8 (avg)	72.2	1-3/16
5/25/79	B-2	69.8	1 (avg)	70.9	5/8
5/26/79	B-2	68.9	3/4 (avg)	70.6	1
6/27/79	C-1	81.9	5/8	75.7	5/8
6/29/79	C-1	83.9	9/16	84.7	1-1/8
6/29/79	C-1	82.8	11/16	76.1	9/16

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